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#147

Gel'man, A.B
To

GEL'MAN, A. B.

GEL'MAN, A. B. - "Mineral nutrition and the mineral content of milk in feeding high-yield cows according to the system used at the Vologda Experimental Animal Husbandry Station". Leningrad, 1954. Min Higher Education USSR. Leningrad Agricultural Inst. (Dissertation for the degree of Candidate of Agricultural Sciences).

SO: Knishnaya Letopis' No. 46, 12 November 1955. Moscow

a-3

BC

Synthesis compounds of platinum. A. GELMAN
(Sov. Rep. Leningrad State Univ., 1960, 2, No. 2,
5-67).— C_2H_4 is passed through eq. K_2PtCl_6 for
15 days at room temp. and eq. $Pt(NH_3)_4Cl_2$ is added.
This reacts with $[Pt(C_2H_4)_2Cl_2(PtNH_3)_2]$ to yield $[Pt(C_2H_4)_2Cl_2(PtNH_3)_2]$ (I), identical with that obtained by Selig from Na_2PtCl_6
with H_2PtCl_6 , to yield $[Pt(C_2H_4)_2Cl_2(PtNH_3)_2]$ (II) to
and HNO_3 . $[Pt(C_2H_4)_2Cl_2(PtNH_3)_2]$ reacts with HCl to
afford $NH_4[Pt(C_2H_4)_2Cl_2]$ and with CH_3NH_2 (III) to
give $PtCl_2(NH_3)(CH_3NH_2)$ (IV), indicating its cis configuration.
An attempted prep. of the trans-isomeride by Jørgen-
sen's method was unsuccessful. (I) in dil. HCl and
 C_2H_4 yield cis- $[Pt(C_2H_4)_2Cl_2(PtNH_3)_2]$ (V), converted
by HCl into $C_2H_5[NH_4][Pt(C_2H_4)_2Cl_2]$ (VI) by (II) into
(VII), and by action of $C_2H_5NH_2$ into trans-
 $[Pt(C_2H_4)_2Cl_2(PtNH_3)_2]$ (I) and $[Pt(C_2H_4)_2Cl_2(PtNH_3)_2]Cl_2$ give
 $[Pt(C_2H_4)_2Cl_2(PtNH_3)_2]$ (I). The salts
 $[Pt(C_2H_4)_2Cl_2(PtNH_3)_2]Br_2$, $C_2H_5NH_4[Pt(C_2H_4)_2Cl_2]$, and
 $[Pt(C_2H_4)_2Cl_2(PtNH_3)_2]X$ are described. The stability
of salts of the series $[Pt(C_2H_4)_2Cl_2(PtNH_3)_2]X$ rises in the series
 $R = (II) < NH_4^+ < C_2H_5^+ < quinoline$, and $X =$
 $CN^- < OCN^- < NO_3^- < I^- < Br^- < Cl^-$. R.T.

ASG-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ADDRESS		PROCESSES AND PROPERTIES INDEX	
BC		C-3	
<p>Isomerism of ethylene compounds of platinum. I. I. TCHERNIAKOV and A. D. GELMAN (Compt. rend. Acad. Sci. U.R.S.S., 1954, 4, 181-184).—By treating K₂PtCl₆ with C₂H₄ and then with NH₃ or C₂H₄ (A, trans-[C₂H₄PtCl₂]) is formed, contrary to the expected rule. A cis-compound was obtained by passing C₂H₄ through a solution of a Pt(NH₃)₂Cl₂ (M = methyl). These results are ascribed to the great trans-influence of C₂H₄. B. C. H.</p>			
<p>ABB-11A METALLURGICAL LITERATURE CLASSIFICATION</p>			
SOURCE SYMBOL		COLLECTION	
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100		1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100	

Hydrazine compounds of platinum. I. I. TCHERNIAEV and A. D. GILMAN (Ann. Soc. Platin., 1937, 36, 77-121). K_2PtX_6 (I) in 3-5% HCl and $\text{C}_2\text{H}_5\text{NH}_2$ react at room temp. as follows ($\text{X} = \text{Cl}, \text{Br}$): (I) + $\text{C}_2\text{H}_5\text{NH}_2 \rightarrow \text{K}[\text{Pt}(\text{C}_2\text{H}_5\text{N}_2\text{X})_2]$ (II) + KCl . (II) reacts with $(\text{F}_2\text{H}_2\text{X})_2$ to give $(\text{F}_2\text{H}_2\text{N})_2[\text{Pt}(\text{C}_2\text{H}_5\text{N}_2\text{X})_2]$ (M = $\text{NH}_4, \text{C}_2\text{H}_5\text{NH}_3$), and with H to afford the compounds $[\text{Pt}(\text{C}_2\text{H}_5\text{N}_2\text{X})_2]$. The equilibrium $[\text{Pt}(\text{C}_2\text{H}_5\text{N}_2\text{X})_2] \xrightleftharpoons[\text{H}]{\text{HX}}$ $\text{MM}[\text{Pt}(\text{C}_2\text{H}_5\text{N}_2\text{X})_2]$ is shown to exist, and the products are isolated and described. The $\text{C}_2\text{H}_5\text{N}_2$ complexes behave analogously to other Pt complexes; they are stable in dry air, and in light, but are instantly decomposed by neutral or alkaline aq. solutions, with production of Pt . The stability of the complexes rises in the series $\text{M} = \text{CH}_3\text{NH}_3 < \text{NH}_4 < \text{C}_2\text{H}_5\text{NH}_3 < \text{quinoline}$, and $\text{X} = \text{CN} < \text{CNS} < \text{NO}_2 < \text{I} < \text{Br} < \text{Cl}$. Attempts to determine the configuration of the complexes were unsuccessful, owing to their instability. R. T.

B. T.

PROCESSING AND PROPERTIES INDEX

A-1

B-1

Compounds of platinum with unsaturated hydrocarbons of the ethylene series. A. D. GRIMAN. (Compt. rend. Acad. Sci. U.R.S.S., 1937, 16, 351—354; cf. A., 1937, II, 54).—Replacing Cl by Br, or C_2H_5 by propylene, isobutylene, or styrene, prep. and properties are given for further members of the complex type: $[C_2H_4, X PtCl_2]$ where $X = NH_2$ or C_2H_5N . As with the chlorides, *trans*-forms are obtained from Zeise type salts, *cis*- from Coas type. $[C_2H_4, X PtCl_2]$ with KBr yield the bromides. The chlorides are inter-replaceable, showing residual affinities in the order $C_2H_4 > C_2H_5 > C_2H_5$ or C_2H_5 (cf. A., 1936, 1000). $[C_2H_4, NH_2 PtCl_2]$ when boiled with HCl yields Coas' salt, showing elimination of C_2H_4 to be the primary reaction. The results confirm the *trans*-influence in the inner shell of the unsaturated mole.

I. McA.

METALLURGICAL LITERATURE CLASSIFICATION

CLASSIFICATION										COLLECTION									
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20

The isomerism of ethylene chloride compounds of platinum. I. J. Chernavsky and Anna D. Hoffman. *Jour. veter. Platin.*, *Ind. chim. (U. S. S. R.)* No. 13, 5-12 (1948); cf. *J. C. I.* 32, 445.—When K_2PtCl_6 is treated with C_2H_4 and then NH_3 , *trans*- $PtCl_2(H_2C=CH_2)NH_3$ is formed. When NH_3 ($PtNH_3Cl_2$) is treated with C_2H_4 , only the cis isomer can be formed, since the ClOxosate the NH_3 is strongly held by the trans effect. Actually, a yield of 70% of the cis isomer (II) of I is obtained. II decomps. and deposits a Pt mirror after 5-6 min. in boiling H_2O , gives a ppt. with $AgNO_3$ and reacts with CS_2NH_3 to form $[Pt(CS_2NH_3)_2]Cl_2$. Its soly. at 25° is 0.233 g. per 100 cc. H_2O and 0.1280 g. per 100 cc. $FIOH$. In an analogous way, $pyH[PtPyCl_2]$ and C_2H_4 give 50% C_2H_4 - $ClpyClPt$, decomps. about 160°, which has properties similar to those of II. Its soly. at 25° is 0.056 g. per 100 cc. H_2O and 0.0573 g. per 100 cc. 90% $FIOH$. When II is dissolved in NH_4OH , the C_2H_4 is replaced by NH_3 . Thus, when C_2H_4 is added to a Pt compl. contg. an amine in the inner sphere, a cis compl. is formed, but if the amine is added to a Pt compl. with C_2H_4 in the inner sphere, the trans isomer results. H. M. Leicester

H. M. Lempert

ADDITIONAL METALLURGICAL LITERATURE CLASSIFICATION

Compounds of platinum and carbon monoxide. Anna D. Hoffman and M. Bauman. *Compt. rend. acad. sci. P. R.* 20, 18, 615-6, 1918 (in English), *cf. C. A.* 32, 2881. It and it prepd the following compds: $\text{PtCl}_2 \cdot \text{CO}$, $\text{PtCl}_2 \cdot 2\text{CO}$ and $2\text{PtCl}_2 \cdot 3\text{CO}$ previously described by Pullinger (*Ber.* 20, 229 (1891)). They also prepd $\text{PtCl}_2 \cdot \text{CO} \cdot 2\text{NH}_3$, $\text{PtCl}_2 \cdot 2\text{CO} \cdot 2\text{NH}_3$, and $\text{PtCl}_2 \cdot \text{CO} \cdot 2\text{NH}_3$ by passing NH_3 and C_2H_2 into CCl_4 solns of the above-mentioned compds. The first mentioned group of compds was prepd. by the action of CO for 7-14 days at room temp. on a soln. of K or NH_4 chloroplatinate. The color of the solns gradually turned yellow and a cherry-red film formed at the surface. Addn. of an aq. pyridine (Py) dropwise to the greenish-yellow filtrate which probably contained $\text{K}(\text{PtCOCl}_4)$ yielded a yellow ppt. according to the following equation: $\text{Me}(\text{PtCOCl}_4) + \text{Py} \rightarrow (\text{PtCOPyCl}_4) + \text{MeCl}$.

MeCl . Reppn. of the crude product from a HCl soln. yielded a pure product of the compd. indicated by the formula in the equation. The yield is 30.4% theory and Cl detn. by the ordinary method accounted for only 7% total halogen. However, when the substance was slowly reduced by Mg in acetate soln. 17.41% Cl was obtained (theoretical Cl 19.02%). PtCOPyCl_4 is lemon-yellow in color and is decompd. by H_2O into Pt , CO , C_2H_2 and HCl . Its soly. in EtOH at 25° is 0.060 g. per 100 cc. and it melts with decompn. at $127-29^\circ$. It dissolves in d^5HCl and evapn. of the soln. yields crystals analyzing $\text{PyH}(\text{PtCOCl}_4)$ and is identical with the compd. described by Mylius and Baeyer (*Ber.* 20, 2424 (1891)). Addn. of

C_2H_2 gives rise to a ppt. of the original substance $\text{PtCO} \cdot \text{PyCl}_4$. Thus, by analogy with the behavior of the C_2H_2 type complex, the latter substance exists in the trans form $\text{CO} \cdots \text{Cl}$.

The formation of the trans isomer $\text{Pt} \cdots \text{Py}$ when a soln. of Koss' salt is treated with CO proves that C_2H_2 and CO compds. of Pt are perfectly analogous to each other. Koss' Py salt yielded too small a quantity of the substance for investigation. With Koss' NH_3 salt beautiful pale yellow crystals of $(\text{PtNH}_2\text{ClCOCl})$ sep'd. after 6-10 days according to the equation: $\text{NH}_4(\text{PtNH}_2\text{Cl}_4) + \text{CO} \rightarrow \text{NH}_4\text{Cl} + \text{PtNH}_2\text{ClCOCl}$. This reaction is very sensitive to temp.; normally it occurs only within the limits $11-13^\circ$. This substance presented no difficulty in its detn. of Cl content and according to the conditions of its prepn. (Chernyshev and Holman, *C. A.* 31, 2541) it has the cis form. It differs very markedly from the previously described substance, melting with decompn. at $180-185^\circ$; soly. in EtOH , 0.025 g. in 100 cc. soln. Thus, it has been established that CO just as C_2H_2 and its homologs has a high trans influence in the complex. On this basis the cis and trans carbonyl-amine dichloride of Pt having a compn. $(\text{PtNH}_2\text{ClCOCl})$ forms have been prep'd. An attempt has been made to explain the high trans influence of CO and also the trans influence of C_2H_2 and NO , through the fact that the C and N atoms are unsat'd.

W. A. Cook

10

Stability of coordinated ethylene hydrocarbons. Anne
L. Hedvorn. *Compt. rend. acad. sc. U. R. S. S.* 20, 307
10(1938) (in English).—The stability decreases according
to the sequence: styrene, C_6H_6 , C_6H_4 , C_6H_2 . CO has a
greater stability than any of these. Greg M. Evans

ASAC-SLA METALLURGICAL LITERATURE CLASSIFICATION

BC

Compounds of platinum (series) with ethylene hydrocarbons. A. G. Collins (Ang. Syst. Platin., 1968, No. 20, 22-23;—R₂PtCl₂ and CH₂RCH₂, give complexes of the type R[PtCl₂(CH₂CH₂)], converted by aq. NH₃ or C₂H₄ into [PtCl₂NH₃(OH)(OR)] or [PtCl₂C₂H₄NH₃CONH₂] (R = Me, Et, Ph); [PtCl₂C₂H₄XN₃], is a by-product in the case of CH₃COCH₃. NH₃[PtBr₂(NH₃)] and C₂H₄ affords cis- and trans-[PtBr₂(NH₃)₂(C₂H₄)]; cis- and trans-[PtBr₂(O₂N)₂(C₂H₄)] are prepared analogously.

R. T.

PROCESSING AND PROPERTY DATA

24

Ethylene nitrochlorides of platinum. Anna I. Litvin
man and I. B. Litvin. *Ann. Inst. Platine, Inst. Chim.
Petro. (U. S. S. R.)* No. 10, 20 (1959). $\text{PtCl}_2(\text{C}_2\text{H}_4)_2$
is best prepd. by refluxing Na_2PtCl_6 for 6-8 hrs. with aq.
EtOH and adding KCl. Excess K_2PtCl_6 pptd. and the
nitrate is evaporated in a vacuum until certain begins. The
salt can be purified by fraction with pyridine and reprecipitation
with HCl. When 1 mol. of this salt reacts with 2
mols. of NaNO_2 , C_2H_4 splits out and $\text{Na}_2[\text{Pt}(\text{NO}_2)_2\text{Cl}_2]$ is
formed. If the proportions are mol. for mol., the product
is $\text{Na}_2[\text{Pt}(\text{C}_2\text{H}_4)(\text{NO}_2)_2]$, which is very sol., but reacts with
 C_2H_4 and NO_2 groups are in the trans position in spite of
the strong labilizing effect which each exerts. However,
owing to this, the complex reacts with pyridine to form
 $[\text{Pt}(\text{C}_2\text{H}_4)(\text{py})_2]$. Attempts to prep. a nonelectrolyte
contg. C_2H_4 and NO_2 by treatment of $[\text{Pt}(\text{NH}_3)_2\text{C}_2\text{H}_4\text{Cl}_2]$
with NaNO_2 , or of $\text{NH}_4[\text{Pt}(\text{NO}_2)_2\text{Cl}_2]$ with C_2H_4 , were
unsuccessful. Complexes of C_2H_4 or C_2H_4 with NiCl_2 ,
 $\text{Co}(\text{NO}_2)_2$ or $\text{Ni}(\text{CN})_2$, NH_4Cl could not be obtained.
H. M. Leicester

AND S.E.A. METALLURGICAL LITERATURE CLASSIFICATION

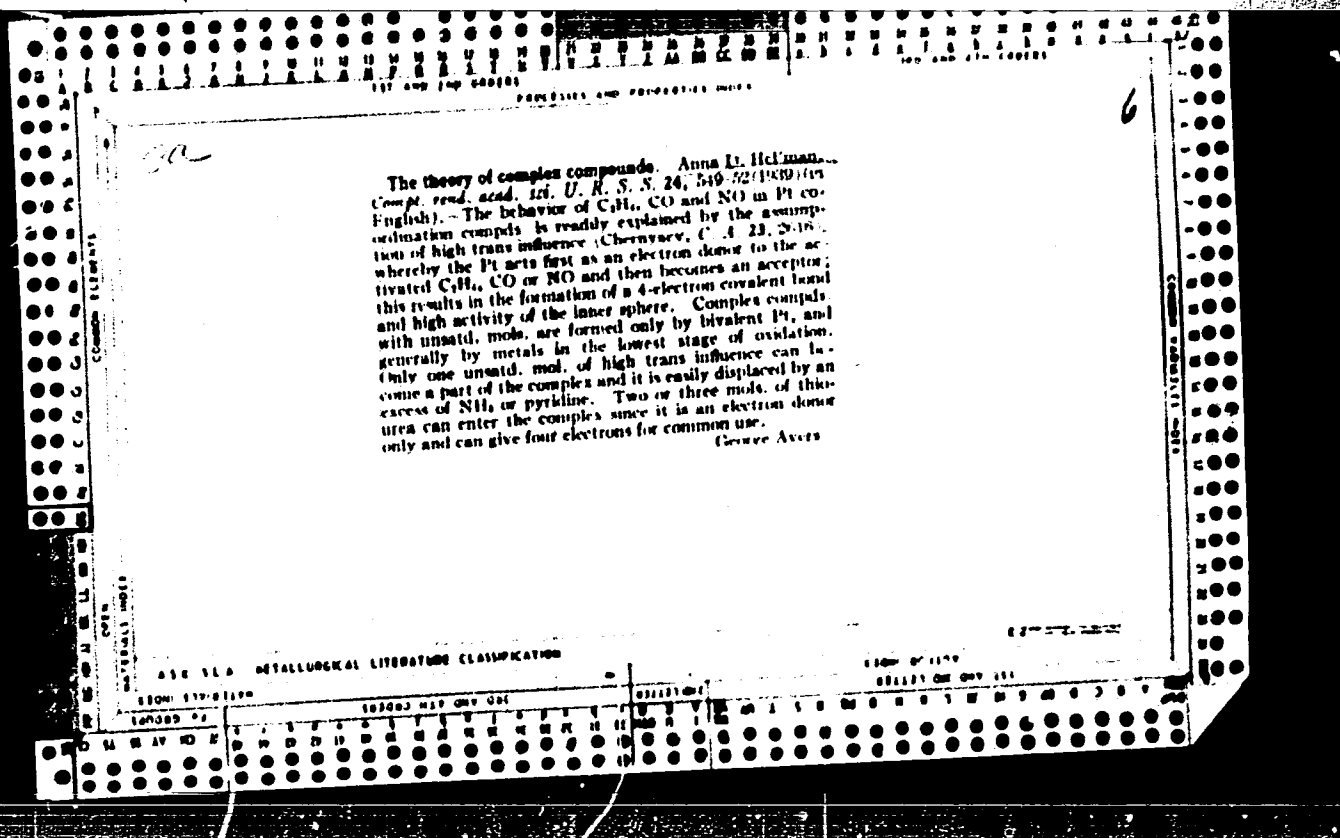
BC

R-1

Mixed platinum dichlorodiammines possessing a cis-configuration. A. GELMAN (Osmot. rend. Acad. Sci. U.S.S.R., 1960, 28, 107—110).—Unlike the case previously recorded (Tishchenov and Gelman, A., 1960, I, 94), introduction of NH₃ into NH₂[Pt(C₂H₅N)₂Cl₂] and C₂H₅N into NH₂[Pt(NH₂)₂Cl] leads in each case to cis-NH₂[Pt(NH₂)(C₂H₅N)Cl₂] (conductance at 25° recorded), which with aq. NH₃ gives NH₂[Pt(NH₂)(C₂H₅N)Cl], with Cl₂, followed by C₂H₅N yields NH₂[Pt(C₂H₅N)₂Cl₂], and with CS(NH₂)₂ gives Pt[CS(NH₂)₂]₂Cl₂, which with K₂PtCl₆ affords Pt[CS(NH₂)₂]₂PtCl₆. F. R. O.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

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10000 0 5	10000 0 5	10000 0 5
10000 0 6	10000 0 6	10000 0 6
10000 0 7	10000 0 7	10000 0 7
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6

Nitrosyl compounds of platinum. A. D. Helman and
 Z. P. Alakumova. *Compt. rend. acad. sci. U. R. S. S.* 24,
 748-51 (1969). (in English). On allowing a sat'd soln. of
 K or NH₄ chloroplatinite to stand 3-4 days in a NO atm.,
 a green soln. (I) formed, apparently containing the ion Pt-
 NOCl₂⁺. Addn. of [Pt(NH₃)₄]Cl₂ soln. to I gave a red-
 dish gray ppt. of [Pt₂(NH₃)₄](PtNOCl₂)₂. Adding pyridine
 to I gave an immediate ppt. of PtNOpyCl₂ (II) (green).
 Dissolved in pyridine, II gave a yellow ppt. of Ptpy₂Cl₂
 which reacted with thiourea to give *trans*-Ptpy₂th.
 Hence II has a *trans* configuration. NO does not react
 with chloroplatinite. A. O. Allen

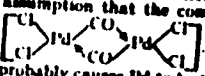
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Ca

Valency of platinum in ethylene complex compounds.
A. D. Il'kman and D. I. Ryabchikov. *Compt. rend. acad. sci. U. R. S. S.* 33, 402-3(1911). The results obtained by subjecting Conna's salt, $\text{NH}_4[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$, and Zeise's salts of the type $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ to electrostatic titration with KMnO_4 in acid soln. establish the quadrivalency of Pt in the latter. I, in which Pt is bivalent, is oxidized normally and a jump in the potential is observed at the transition point. With II the initial potential of the soln. is 650-700 mv., which is characteristic of Pt (IV) compds., and no oxidation occurs.

J. C. Lo Cicero

ASS-SLA METALLURGICAL LITERATURE CLASSIFICATION

Compounds of palladium with carbon monoxide. A. Gelman and E. Meilach (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 28, 171-174). By passage of CO for several days through $(\text{NH}_4)_2\text{PdCl}_6$ in conc. HCl the compound obtained is not $\text{NH}_4[\text{PdCl}_5\text{CO}]$ but $\text{NH}_4[\text{PdCl}_4\text{CO}]$. By metathesis reactions with $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]$ and with $(\text{CH}_3)_3\text{NH}[\text{PtCl}_6]$ the compounds $[\text{Pt}(\text{NH}_3)_4][\text{PdCl}_4\text{CO}]_2$ and $(\text{on } \text{H}_2)[\text{PdCl}_4\text{CO}]_2$ have been isolated. The structure of these compounds is discussed in terms of the co-ordination theory, and formulae are advanced on the assumption that the compounds are dimers containing the ion . The instability of the Pd carbonyl halides probably causes Pd to be tervalent in these compounds. J. O'M-B.

Synthesis of chloroammine complexes of platinum with four different substituent groups in the inner sphere. A. Gelman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **28**, 310-313). The geometrical isomers NiH_2Cl_2 (I) and NiH_2Cl_2 (II) have the following properties: (I), greenish yellow prismatic crystals, n_D^{20} 1.743, n_D^{25} 1.738, insol. in cold HCl, decomposed by cold AgNO_3 ; (II), yellow crystals, n_D^{20} 1.743, n_D^{25} 1.708, sol. in cold HCl giving $\text{NiH}_2[\text{Cl}(\text{C}_6\text{H}_5)_2]\text{Cl}$, giving a very feeble opalescence with cold AgNO_3 . Attempts to obtain the anion $[\text{Pt}(\text{C}_6\text{H}_5)_2\text{Cl}]^-$ led to displacement of C_6H_5 from the complex. L. J. J.

25

781. Complex Compounds of Platinum with Unsaturated Molecules. (In Russian.) Anna Gelsman (Nikhtina) 100 pages, 1945. Academy of Sciences of U.S.S.R., Institute of General and Inorganic Chemistry, Moscow.

After a short literature review of the complex ethylene compounds of platinum, a number of these reactions are investigated in order to test the validity of a theory advanced by Tschuganov and others. Finally, the author proposes a new theory concerning reactions of unsaturated molecules with platinum. 113 ref.

ASAC SLA METALLURGICAL LITERATURE CLASSIFICATION

Compounds of platinum with carbon monoxide. A. D. Gel'man. *Ann. sekv. platine, Int. chim. gen. (U.S.S.R.)* 18, 50-59 (1945) (in Russian).—Sols. of K or NH₄ chloroplatinate(II), kept in contact with CO at room temp. for 7-14 days, formed gradually, besides a small amt. of a cherry red Pt contg. sediment, a green-yellow filtrate from which dropwise addn. of pyridine (py) (under const. cooling with ice water) pptd. a yellow solid according to $K_2[PtCl_6] + py = KCl + [PtCO(py)Cl_5]$ (I) with a yield of 30-40%. On decompn. with hot water, AgNO₃ ppts. only about 1/2 of the Cl in I; nearly theoretical ptn. of Cl is attained only after slow reduction with Mg in AcOH. The compd. fm. 127-0° with decompn.; solv. in EtOH 0.009 g./100 ml. at 25°; from a soln. of I in HCl, evapn. yields $pyH[PtCOCl_5]$ (II) which is readily reconverted into I by py. From the reversibility I \rightleftharpoons II, it follows that in I the two Cl must be in trans positions relative to each other, CO trans to py.

The analogy of the Pt-py complex with the corresponding Pt-C₆H₅ complexes demonstrated by the reaction $NH_4[PtNH_2Cl_5] + CO \rightarrow NH_4Cl + [PtNH_2COCOC]Cl_4$ (III) occurring only within the narrow temp. limits 11-13°; no reaction at all occurs at 0°, at 20° only the cherry red sediment forms. III proves to be a cis compd. by the ready ptn. of all its Cl by AgNO₃ after decompn. with hot water and relatively fast decompn. by cold water; decomp. without m. 180.5°; solv. in EtOH 0.021 g./100 ml.; insol. in HCl; refractive indexes $n_D^{20} 1.700$, $n_D^{25} 1.745$, $n_D^{30} 1.722$, $D_4^{25} 1.27$. Consequently, replacement of NH₂ by py results in a change of configuration which alone can account for the considerable difference of the properties of I and III. From a const. soln. of II, $[PtNH_2COCOC]Cl_4$ ppts. a compd. shown to be $[Pt(NH_2)[PtCOCl_5]$ (IV) in an indirect way: $IV + K_2PtCl_6 = [Pt(NH_2)[PtCl_5]Cl_2]$ (Magnus' green salt) + $2 K[PtCOCl_5]$, and $2 K[PtCOCl_5] + 2 py = 2 I + 2 KCl$; yield in IV, after washing with ether and drying, 88.5%. Treatment of I with III gives $pyH[PtCOBr_5] \cdot H_2O$. The high trans influence of both C₆H₅ and CO, which cannot be explained by a dipole moment effect, might be tentatively ascribed to the unsat. of C; this is borne out by the absence of complex formation with satd. hydrocarbons, and is paralleled by the trans influence of the NO₂ group. N. Thon

PROCESSIES AND PROPERTIES INDEX

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Compounds of platinum with nitric oxide. A. P. Golman and Z. P. Maksimova. *Dokl. Akad. Nauk SSSR*, 18, 61 (1945) (in Russian). - chem. rev. (U.S.S.R.) 18, 61 (1945) (in Russian). - From air-free satd. solvs. of K or NH₄ chloroplatinate (II), kept in contact with NO at room temp., a red-brown ppt. begins to form after 10-12 hrs., and the pptn. is complete after 3-4 days. The compl. pptd. was identified as [Pt(NOCl)] (I) by: (1) its reaction with Pt(NH₃)₄Cl₂, K[Pt(NOCl)] (II) resulting in pptn. of [Pt(NH₃)₄][Pt(NOCl)₂] (III), confirmed by analysis; and by the reaction II + K₂[Pt(NOCl)] [Pt(NH₃)₄][PtCl₂] (Maignus' green salt) + 2K[Pt(NOCl)] (yellow-gray filtrate); (2) pptn., by dropwise addn. of pyridine (py), of [PtNO(py)Cl] (III'), confirmed by analysis. In analogy with the corresponding CO compl. analog (cf. the foregoing abstract), only about 1% of the Cl can be pptd. by AgNO₃ after decomp. of the complex; fusion with Na₂CO₃ yields only a little more precipitable Cl than reduction with Zn + H₂SO₄; the amt. is somewhat increased by previous oxidation with H₂O₂. Microscopic examn. shows the presence of 2 phases, one with n_D^{20} = 1.785, n_a = 1.650, the other n_D^{20} = 1.785, n_a = 1.678. The compl. III is light green; with warm HCl it reacts reversibly according to III $\xrightleftharpoons[\text{py}]{\text{HCl}}$ py H[Pt(NOCl)], which proves its trans configuration; this is further demonstrated by the reactions III + py = [Pt(py)₂Cl]₂ + NO followed by [Pt(py)₂Cl]₂ + 2CS₂(NH₄)₂SO₄ = [Pt(py)₂(SO₄)₂]Cl₂, confirmed by analysis; further by the absence of elec. cond. due to electrolytic ionization. III is readily sol. in warm EtOH, is not decompd. by hot water, and moisture-stable. Attempts to synthesize the cis compl. [Pt(NOCl)(py)Cl] were unsuccessful. Likewise, NO did not react with chloroplatinate(II) solns. (mexpts. extended over 2 weeks). While this neg. result can easily be explained by the lusteris. : of N₂O and CO, which also is inactive, Ni, even though it is isosteric with Co, had no effect on chloroplatinate(II) even under several tens of atm. pressure, in expts. extending over 1½ months. Neither was any reaction observed between N₂ and K[PtCl₂H₂Cl] and K₂CIPtCl₂H₂ CIPtCl₂ except that the butadiene salt was converted into K[PtCl₂H₂Cl], very likely owing to the mere effect of the pressure. N. Thorpe

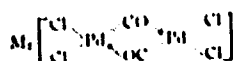
GELMAN, A.		PROCESSING AND PROPERTIES INDEX	
<p>Complex compounds of platinum with acetylene derivatives. A. Gelman, S. Bukhovets, and E. Melnikh. <i>Doklady Akad. Nauk S.S.S.R.</i> 46, 110-12 (1945); <i>Compt. rend. acad. sci. U.R.S.S.</i> 46, 105-6 (1945) (in English). - A concn. aq. soln. of K_2PtCl_6 was heated with 2,5-dimethyl-3-hexyne-2,3-diol (Un) to form water-sol. $K_2[PtUnCl_4]$, which was not isolated but was treated with pyridine to form $[PtUnPyCl_3]$ (I), pptd. as an oil under going crystn. on cooling and scratching with a glass rod. Cryst. I m. 98-7° (open tube) and 101-1° (sealed tube). decomposes in hot water and reacts with thionine to form $[Pt[SC(NH_2)_2]_2Cl_2]$. The mol. wt. of I, detd. cryoscopically in benzene soln., was 690.3 (calcd. 687.36). The properties of I suggest that it exists in the trans configuration. J. W. Perry (lon).</p>			
<p>ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION</p>			
<p>SECTION 1</p>		<p>SECTION 2</p>	
<p>SECTION 3</p>		<p>SECTION 4</p>	

GELMAN, A. D.

The production of complex platinum compounds with ethylenes in the cation. A. D. Gelman and E. A. McClatch, *Comp. rend. acad. sci. U.S.S.R.* 51, 207-8 (1946); cf. *C.A.* 37, 6870 (1943).—A Pt compd. was prepd. as follows: $\text{cis-}[\text{PtCl}_2(\text{C}_2\text{H}_4)\text{NH}_3]^+$, by treatment with AgNO_3 , gave a nitrate-chloro compd., in which the low coordination strength of the NO_3 group makes the mol. readily hydrolyzable: $[\text{PtCl}(\text{NO}_3)\text{NH}_3(\text{C}_2\text{H}_4)] + \text{H}_2\text{O} \rightarrow [\text{PtCl}(\text{H}_2\text{O})\text{NH}_3(\text{C}_2\text{H}_4)] + \text{NO}_3^-$. This product did not crystallize well and was unstable, but when an equimol. amount of pyridine was present, $[\text{PtCl}(\text{C}_5\text{H}_5\text{N})\text{NH}_3(\text{C}_2\text{H}_4)]\text{NO}_3$ was formed; snow-white, crystalline, very sol. in H_2O . On standing it gradually darkens and turns dirty gray. In soln. the introduction of Cl^- or Br^- reverses the reaction, giving I, in accordance with Chertnyakov's rule (*C.A.* 30, 60889). A. S. Pastman

CA

Theory and practice of complex compounds of platinum with unsaturated molecules. Anna Gel'man and E. A. Melnikh. *Izvest. Sektora Platin* 1st Div. *Blagovest. Metal.* Inst. Obshch. i Neorg. Khim., Akad. Nauk S.S.S.R. (Ann. sector platine, Inst. chim. gen.) No. 20, 21-41 (1947).—Ethylenediamine was added dropwise to an aq. soln. of $K_2[PtCl_4]$ forming instantaneously a faint yellow ppt. of $(PtCl_2)_2 \cdot C_2H_4 \cdot N_2$. In this reaction the $C_2H_4 \cdot N_2$ did not close a ring; it acted as bridge between 2 Pt atoms. Pt acetyl chloride formed a compl. with $C_2H_4 \cdot N_2$ in which Pt atoms were connected on one side by C_2H_4 and on the other by $C_2H_4 \cdot N_2$. Attempts to form a Pt ethylene trihalide comp. Cl, Br, and I were unsuccessful. This is attributed to the facts that I is in the trans position to C_2H_4 and both Cl and Br compete on the same ordinate for a covalent link with Pt. From the NH_4 salt of $PtNH_2Cl$, the cis and trans isomers of $PtCl_2 \cdot BrNH_2 \cdot Cl$ were produced. The action of CO on a satd. soln. of $(NH_4)_2PtCl_6$ yielded $NH_4[PtCOCl_3]$ (1). The correctness of this formula was confirmed by causing 1 to react with $[Pt(NH_3)_4]Cl_2$ and with ethylenediamine hydrochloride. The reaction products were $[Pt(NH_3)_4][PtCOCl_3]$ and $(C_2H_4NH_2)_2[PtCOCl_3]$, resp. The Pd carbonyl chloride is assigned the structure



Expts. on pptg. Pd and Pt from pure solus., slimes, and sulfate solus. of Ni and Cu by reducing the noble metals with C_2H_4 , gave satisfactory results. The nature of Pt and Pd complexes with ethylenic compds. indicates that the complexes are not coordination compds. but rather covalent. M. Hosh

GEL'MAN, A.

PA 58T12

USSR/Chemistry - Platinum Compounds
Chemistry - Isomers

Jan 1947

"The Formation of the Third Isomer of Ethylene-Ammonia-Chloride-Bromide Platinum," A. Gel'man, Ye. Gorushkina, Inst Gen and Inorg Chem imeni N. S. Kurnakov, Acad Sci USSR, 3 pp

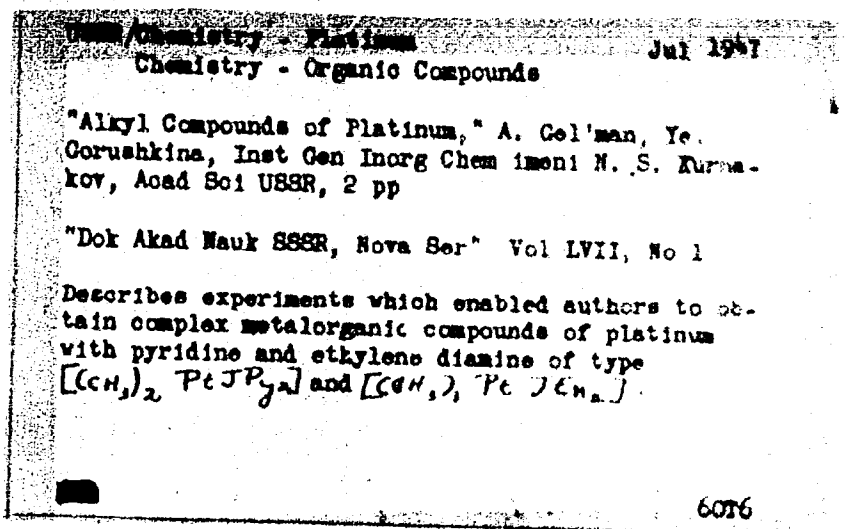
"Dok Akad Nauk SSSR, Nova Ser" Vol LV, No 1

Describes experiments in which it was found possible to synthesize third isomer of ethylene-ammonia-chloride-bromide platinum; possible only after forming a group of atoms with ethylene in a cation. Submitted by Academician I. I. Chernyayev, 3 Jul 1946.

58T12

GEL'MAN, A.

PA 6076



CA

The production of alkyl compounds of platinum from Zeise's salt. Anna D. Gal'ina and R. A. Gerasimova. Doklady Akad. Nauk S.S.S.R. 37, 240 (1917). (Chem. Zentr. (Russian Zentr. Ed.) 1948, 1, 1267. The Pt in the ethylene salts of Zeise is to be regarded as quadrivalent. Attempts to replace the C_2H_4 by NH_3 , pyridine, NO_2^- , or CN^- have yielded compds. withivalent Pt, the salt Me_2Pt (in which the Pt is quadrivalent) was successfully prepd. by the action of MeMgI on the Zeise K salt, $\text{K}[\text{PtC}_2\text{H}_4\text{Cl}_2]$. The MeMgI was prepd. from 3 g. $\text{Mg} + 30 \text{ g. MeI}$ in 50 cc. ether. C_2H_4 (100 cc.) was added, then 10 g. $\text{K}[\text{PtC}_2\text{H}_4\text{Cl}_2]$ in small portions, next HCl to dissolve the $\text{Mg}(\text{OH})_2$, and the compd. recrystl. from hot C_2H_4 in the usual manner. Derivs. prepd. in like manner were: $[\text{Me}_2\text{Pt}(\text{C}_2\text{H}_4\text{N})]$, $[\text{Me}_2\text{Pt}(\text{NH}_3)_2]$, $[\text{PtMe}_2\text{SO}_2]$, and Me_2PtCl_2 . M. G. Moore.

Inst. Gen. Inorg. Chem. Acad. Sci. USSR

GEL'MAN, A. D.

USSR/Chemistry - Platinum
Chemistry - Isomers

Nov 48

"Obtaining ($\text{H}_3\text{C}_2\text{H}_5\text{ClBrPt}$) in the form of Three
Repeated Isomers," A. D. Gel'man, Ye. F. Karandashova
I. N. Kosen, Inst of Gen and Inorg Chem Acad N. S.
Kurnakov, Acad Sci USSR, 4 pp

"Dokl Ak Nauk SSSR" Vol XLIII, No 1

Studied problem of obtaining three expanded isomers
of a complex compound of bivalent platinum with the
most typical intrasphere substituents (pyridine,
acetonide, chlorine, bromine), using I. I. Chernyayev's
law. Analyzed trans- and cis-isomers and tabulated

61/49717

USSR/Chemistry - Platinum (Contd)

Nov 48

the properties of the three isomers. Submitted by
Acad I. I. Chernyayev 26 Jan 48.

61/49717

ARMENIAN, A. D.

21425 GELMAN, A. D.; FUKHOVETS, S. P.; ILLIASH, I. A.

Kompleksnye soedineniya platiny s proizvodnymi atsetilena.
Soodshch. i. Izvestiya Sektora Platiny i Drugikh Blagorod.
Metallov (In - t Odshchey i Neorgan Khimii im. Kurnakova),
Vyp. 23, 1949, s. 84 - 86.

SC: Letopis' Zhurnal'nykh Statcy, No. 29, Moskva, 1949

GEL'MAN, A.

21/24

GEL'MAN, A. D.; i MEYLANE, E. A.

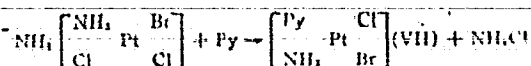
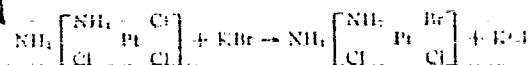
K Polucheniyyu Kompleksnykh Soedineiny Platiny s Etilenom V
Katione. Nazvestiya Sektora Platiny k Drugikh Blagorod.
Metallov (In - t Odshchey i Neorgah, Khimii in. Kurnakova),
Vyp. 23, 1949, s. 87 - 89.

SO: Letopis' Zhurnal'nykh Statey, No. 29, Moskva, 1949

GEL'MAN, A. D.

Production of chlorobromopyridinoamminoplatinum in its three isomeric forms. A. D. Gel'man, G. I. Karalida, I. N. Essen, *Vysokomol. Soedin. i Drugikh Blagorod. Metallov, Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R.* No. 24, 60-71 (1949). — *cis*-[Pt(NH₃)₂Cl]₂ (I) with C₅H₅N gives *cis*-[Pt(NH₃)₂Py]Cl₂ (II). II with HCl gives *trans*-[PtNH₃PyCl₂] (III). III + AgNO₃ + H₂O → [PtPyClNH₃H₂O]NO₃ (IV) + AgCl. IV + KBr → [PtPyBrNH₃Cl] (V) + KNO₃ + H₂O or III + KBr → [PtPyBrNH₃Cl] (V) + 2 V or III + KBr → V + KCl. *trans*-[PtPyBrNH₃Cl] (VI) → 2 V or III + KBr → V + KCl or VI + KCl → V + KBr. Dissolve with heat 1.7 g. I in 3 ml. C₅H₅N and 50 ml. H₂O; cool, filter, add 30 ml. concd. HCl, and heat 3 hrs. under CO₂ atm. Cool, filter, and wash the ppt. until the filtrate is free of Cl⁻. Heat the filtrate with HCl and repeat the preceding operations. Combine the 2 ppts., recrystallize III from hot H₂O, and dry over CaCl₂. By the first method dissolve 0.6310 g. of III in 570 ml. of H₂O. Add 0.2961 g. of AgNO₃ (in soln.), heat, keep in a dark place to settle out, and filter. To the filtrate add

0.2074 g. of KBr, filter, and recrystallize from hot H₂O. By the second method to a hot soln. of III add the required quantity of VI, heat to complete soln., and cool slowly. By the third method dissolve 0.8181 g. of III in approx. 100 ml. of hot H₂O, add 0.2639 KBr, heat to complete soln. in 4-5 hrs., and cool slowly. By the fourth method dissolve 0.5602 g. of VI in 100 ml. of hot H₂O, add 1.008 g. of KCl, heat for approx. 1 hr. at 80-90°, and cool slowly. One of the *cis* isomers was synthesized according to



To obtain the 2nd *cis* isomer dissolve 0.7300 g. of [PtPyCl]₂ in a small vol. of slightly acidified H₂O. Filter and add 0.2939 g. of KBr. Heat over the water bath for 6 min., cool, and add dropwise with stirring 2-3 ml. of 10% NaOH, using 2-3 drops more than the required quantity. Heat for 2 hrs. at room temp. with occasional stirring, cool with ice,

2/2 A.D. GELMAN, E.F. KARASHOVA
& L. N. EISEN

filter, evap. the filtrate, and recrystallize at least twice

from hot H_2O , to obtain $\begin{bmatrix} Py & Si \\ NH_2 & Cl \end{bmatrix}$ (VIII). V.

prismatic, lemon-yellow crystals, $n_D^{20} 1.770$, $n_D^{25} 1.770$, $n_D^{30} 1.767$, soly. in H_2O at 20° 0.019 g./100 g. of soln., decomp.

poses approx. 224° , forms with thiourea $\begin{bmatrix} Thio & Thio \\ Thio & Thio \end{bmatrix}$ X₁.

VII, rhombic, pale-yellow crystals, $n_D^{20} 1.770$, $n_D^{25} 1.769$, $n_D^{30} 1.766$, soly. in H_2O 0.184 g./100 g. of soln., decomp. at ap-

prox. 200° , forms $\begin{bmatrix} Thio & Thio \\ Thio & Thio \end{bmatrix}$ X₂, VIII, light yellow

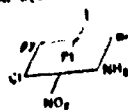
fine-cryst., $n_D^{20} 1.778$, $n_D^{25} 1.762$, $n_D^{30} 1.633$, soly. in H_2O 0.145 g./100 g. of soln., decomposes approx. 165° , forms

$\begin{bmatrix} Thio & Thio \\ Thio & Thio \end{bmatrix}$ X₃.

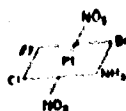
Al. Hensch

CA

Complex compounds of quadrivalent platinum with six different substituents in the inner sphere. A. I. Gel'dman and L. N. Popen (N. S. Kurnakov Inst. Gen. Inorg. Chem. Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 79, 603-8 (1951).—The



isomer of $[Pt(NO_2)_2(CH_3)_2]$ (I) ($\mu = 4.11$) was synthesized by first heating *trans*- $[Pt(NO_2)_2(CH_3)_2]$ with HNO_3 , which yielded

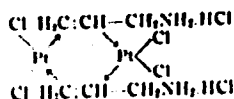


(II), bright-yellow, refractive index $n_D^{20} = 1.782$, $n_D^{25} = 1.775$, $n_D^{30} = 1.768$, $n_D^{35} = 1.761$, $n_D^{40} = 1.754$, $n_D^{45} = 1.747$, $n_D^{50} = 1.740$, $n_D^{55} = 1.733$, $n_D^{60} = 1.726$, $n_D^{65} = 1.719$, $n_D^{70} = 1.712$, $n_D^{75} = 1.705$, $n_D^{80} = 1.698$, $n_D^{85} = 1.691$, $n_D^{90} = 1.684$, $n_D^{95} = 1.677$, $n_D^{100} = 1.670$, $n_D^{105} = 1.663$, $n_D^{110} = 1.656$, $n_D^{115} = 1.649$, $n_D^{120} = 1.642$, $n_D^{125} = 1.635$, $n_D^{130} = 1.628$, $n_D^{135} = 1.621$, $n_D^{140} = 1.614$, $n_D^{145} = 1.607$, $n_D^{150} = 1.600$, $n_D^{155} = 1.593$, $n_D^{160} = 1.586$, $n_D^{165} = 1.579$, $n_D^{170} = 1.572$, $n_D^{175} = 1.565$, $n_D^{180} = 1.558$, $n_D^{185} = 1.551$, $n_D^{190} = 1.544$, $n_D^{195} = 1.537$, $n_D^{200} = 1.530$, $n_D^{205} = 1.523$, $n_D^{210} = 1.516$, $n_D^{215} = 1.509$, $n_D^{220} = 1.502$, $n_D^{225} = 1.495$, $n_D^{230} = 1.488$, $n_D^{235} = 1.481$, $n_D^{240} = 1.474$, $n_D^{245} = 1.467$, $n_D^{250} = 1.460$, $n_D^{255} = 1.453$, $n_D^{260} = 1.446$, $n_D^{265} = 1.439$, $n_D^{270} = 1.432$, $n_D^{275} = 1.425$, $n_D^{280} = 1.418$, $n_D^{285} = 1.411$, $n_D^{290} = 1.404$, $n_D^{295} = 1.397$, $n_D^{300} = 1.390$, $n_D^{305} = 1.383$, $n_D^{310} = 1.376$, $n_D^{315} = 1.369$, $n_D^{320} = 1.362$, $n_D^{325} = 1.355$, $n_D^{330} = 1.348$, $n_D^{335} = 1.341$, $n_D^{340} = 1.334$, $n_D^{345} = 1.327$, $n_D^{350} = 1.320$, $n_D^{355} = 1.313$, $n_D^{360} = 1.306$, $n_D^{365} = 1.299$, $n_D^{370} = 1.292$, $n_D^{375} = 1.285$, $n_D^{380} = 1.278$, $n_D^{385} = 1.271$, $n_D^{390} = 1.264$, $n_D^{395} = 1.257$, $n_D^{400} = 1.250$, $n_D^{405} = 1.243$, $n_D^{410} = 1.236$, $n_D^{415} = 1.229$, $n_D^{420} = 1.222$, $n_D^{425} = 1.215$, $n_D^{430} = 1.208$, $n_D^{435} = 1.201$, $n_D^{440} = 1.194$, $n_D^{445} = 1.187$, $n_D^{450} = 1.180$, $n_D^{455} = 1.173$, $n_D^{460} = 1.166$, $n_D^{465} = 1.159$, $n_D^{470} = 1.152$, $n_D^{475} = 1.145$, $n_D^{480} = 1.138$, $n_D^{485} = 1.131$, $n_D^{490} = 1.124$, $n_D^{495} = 1.117$, $n_D^{500} = 1.110$, $n_D^{505} = 1.103$, $n_D^{510} = 1.096$, $n_D^{515} = 1.089$, $n_D^{520} = 1.082$, $n_D^{525} = 1.075$, $n_D^{530} = 1.068$, $n_D^{535} = 1.061$, $n_D^{540} = 1.054$, $n_D^{545} = 1.047$, $n_D^{550} = 1.040$, $n_D^{555} = 1.033$, $n_D^{560} = 1.026$, $n_D^{565} = 1.019$, $n_D^{570} = 1.012$, $n_D^{575} = 1.005$, $n_D^{580} = 0.998$, $n_D^{585} = 0.991$, $n_D^{590} = 0.984$, $n_D^{595} = 0.977$, $n_D^{600} = 0.970$, $n_D^{605} = 0.963$, $n_D^{610} = 0.956$, $n_D^{615} = 0.949$, $n_D^{620} = 0.942$, $n_D^{625} = 0.935$, $n_D^{630} = 0.928$, $n_D^{635} = 0.921$, $n_D^{640} = 0.914$, $n_D^{645} = 0.907$, $n_D^{650} = 0.900$, $n_D^{655} = 0.893$, $n_D^{660} = 0.886$, $n_D^{665} = 0.879$, $n_D^{670} = 0.872$, $n_D^{675} = 0.865$, $n_D^{680} = 0.858$, $n_D^{685} = 0.851$, $n_D^{690} = 0.844$, $n_D^{695} = 0.837$, $n_D^{700} = 0.830$, $n_D^{705} = 0.823$, $n_D^{710} = 0.816$, $n_D^{715} = 0.809$, $n_D^{720} = 0.802$, $n_D^{725} = 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$n_D^{2995} = 0.000$, $n_D^{3000} = 0.000$, $n_D^{3005} = 0.000$, $n_D^{3010} = 0.000$, $n_D^{$

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Complex compounds of platinum with ethylamine. A. D. Zel'man and L. N. Essen (N. S. Kurnakov Inst. Gen. and Inorg. Chem., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 77, 273-5 (1961). — Reaction of a neutral soln. of K_2PtCl_6 with $CH_3CH_2NH_2$ (I) gives the salt $[PtCl_5]^-$ (II) dark-yellow, stable on heating with H_2O , sparingly sol., dissolving in NH_4OH with a reddish brown color. That soln. in NH_4OH , acidified with HCl , gives with K_2PtCl_6 a dirty-green ppt. of $[(NH_4)_2PtCl_6]$ (III). These reactions prove that in II, the double bond of I takes no part in the complex formation; I is bound to the Pt only by the NH_2 group. Addn. of I to the Pt atom through the double bond takes place on heating in an acid medium or on prolonged reaction at room temp. Thus, heating of a strongly acid soln. of K_2PtCl_6 with I gives a golden-yellow soln., which on cooling ppts. golden-yellow crystals of a dimer $[ClPtCH_2CH_2NH_2]_2HCl_2$ (III); to this the structure



is assigned by analogy with C_2H_4 and $PhCH=CH_2$ complex. Heating with H_2O produces a Pt mirror; this indicates bonding through the double bond. Prolonged heating of III with 10% HCl gives the Zeise-type acid $H[ClPtHCl]$ (IV), which on careful neutralization with 5% $NaOH$ forms a canary-yellow ppt. of $[ClPtH]$ (V), obviously a cyclic complex, $\left[\begin{array}{c} Cl \quad CH_2CH \\ | \quad | \\ Pt \\ | \quad | \\ Cl \quad NH_2CH_2 \end{array} \right]$, giving metallic Pt on boiling with H_2O . This structure is confirmed by the synthesis $NH_4[ClPtCl_2H_2]$ (Zeise's salt) + $HCl \rightarrow NH_4[ClPtHCl]$ + C_2H_4 (evolved), followed by $NH_4[ClPtHCl]$ + $NaOH \rightarrow V$. N. Thon

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Preparation of the three spatial isomers of platinum chlorodipyrithionammine. A. D. Oel'yan and E. P. Karandashova. *Doklady Akad. Nauk S.S.S.R.* 78, 177-80 (1961).—By Chernyshev's rules, synthesis of the trans isomer (T) of $[\text{Cl}(\text{NH}_3)_2\text{pyPt}]$ ($\text{py} = \text{C}_5\text{H}_4\text{N}$) should be feasible

through $\left[\begin{smallmatrix} \text{Cl} & \text{Pt} & \text{NH}_3 \\ \text{py} & & \text{Cl} \end{smallmatrix} \right] + \text{KI} \rightarrow \left[\begin{smallmatrix} \text{Cl} & \text{Pt} & \text{NH}_3 \\ \text{py} & & \text{I} \end{smallmatrix} \right] + \text{KCl}$

the cis(I) isomer (CI) should be obtained through $\text{NH}_3 \left[\begin{smallmatrix} \text{NH}_3 & \text{Pt} & \text{Cl} \\ \text{Cl} & & \text{Cl} \end{smallmatrix} \right] \xrightarrow{\text{KI}} \text{NH}_3 \left[\begin{smallmatrix} \text{NH}_3 & \text{Pt} & \text{I} \\ \text{Cl} & & \text{Cl} \end{smallmatrix} \right] \xrightarrow{\text{py}} \left[\begin{smallmatrix} \text{NH}_3 & \text{Pt} & \text{I} \\ \text{py} & & \text{Cl} \end{smallmatrix} \right]$

and the cis (II) isomer (CII) through $\text{K} \left[\begin{smallmatrix} \text{Cl} & \text{Pt} & \text{Cl} \\ \text{py} & & \text{Cl} \end{smallmatrix} \right] \xrightarrow{\text{NH}_3} \left[\begin{smallmatrix} \text{NH}_3 & \text{Pt} & \text{Cl} \\ \text{py} & & \text{Cl} \end{smallmatrix} \right]$. These theoretically pre-

dicted paths of synthesis were confirmed experimentally. Reaction between trans- $[\text{py}(\text{NH}_3)_2\text{PtCl}_2]$, 0.3-1.0 g., in suspension in 25-75 ml. H_2O , and KI (in 1% excess over the anal. ratio) gave, on $1/2$ hr.'s stirring, yellow-orange prisms of T. A 0.3-1.5-g. sample of $\text{NH}_3[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ in 10-50 ml. hot alc., with the calcd. amt. of KI, changed from golden yellow to dark yellow; dropwise addn. of the calcd. amt. of py gave brown-yellow fine needles of CI. Addn. of the calcd. amt. of KI to $\text{K}[\text{pyPtCl}_3]$ in hot alc. soln., followed by dropwise addn. of 20% NH_4OH , gave yellow needles of CII. The properties of T, CI, and CII, are: refractive indices, n_D^{20} > 1.782, n_D^{20} = 1.78; n_D^{20} > 1.782, n_D^{20} = 1.718; and n_D^{20} > 1.782, n_D^{20} = 1.721; soly. in H_2O at 20°, 0.018, 0.024, and 0.023 g./100 g. concn.; decomps. temp. on heating in a capillary in air, 210, 190, and 170°; reaction with $\text{Cu}(\text{NH}_3)_4^{2+}$ (sh) produces, resp., $\left[\begin{smallmatrix} \text{py} & \text{Pt} & \text{sh} \\ \text{sh} & & \text{NH}_3 \end{smallmatrix} \right] \text{X}_2$ (snow-white), $[\text{Pt}(\text{sh})_2] \text{X}_2$ (yellow), and $[\text{Pt}(\text{sh})_2] \text{X}_2$ (yellow).

N. Thon

1. GEL'MAN, A. D. and KARANDASHOVA Ye. F.
2. USSR (600)
4. Platinum Organic Compounds
7. Reaction of triacidoaminoplatinates of potassium $K[PtNH_2Cl_2X]$ with pyridine, Dokl.AN SSSR 87 No. 4, 1952.
9. Monthly List of Russian Accessions, Library of Congress, February 1953, Unclassified.

GEL'MAN, A.D.

GRINBERG, A.A. (Leningrad); BABAYEVA, A.V. (Moscow); YATSIMIRSKIY, K.B. (Ivanovo); GOREMYKIN, V.I. (Moscow); BOLIY, G.B. (Moscow); FIAL-KOV, Ya.A. (Kiyev); YAKSHIN, M.M. (Moscow); KEDROV, B.M. (Moscow); GEL'MAN, A.D. (Moscow); FEDOROV, I.A. (Moscow); MAKSIMYUK, Ye.A. (Leningrad); VOL'KENSHTeyN, M.V. (Leningrad); ZHDANOV, G.S. (Moscow); PTITSYN, B.V. (Leningrad); ABLOV, A.V. (Kishinev); VOLSHTEYN, L.M. (Dnepropetrovsk); TROITSKAYA, A.D. (Kazan'); KLOCHKO, M.A. (Moscow); BABAYEVA, A.V.; TRONEV, V.G. (Moscow); RUBINSHTeyN, A.M. (Moscow); CHERNYAYEV, I.I.; GRINBERG, A.A.; TANANAYEV, I.V.

Explanation of the transeffect. Isv. Sek. plat. 1 blag. met. no. 28:
56-126 '54. (MIRA 7:9)

(Compounds, Complex) (Platinum)

GEL'MAN, I. D.

Preparation of the complex compounds of quadrivalent platinum with six different hetero ligands
 I. D. Gel'man and A. D. Gel'man. *Dokl. Akad. Nauk SSSR*, 1974, 225, 1384.
 With 6 different substituents were prepared: Cl_2PtCl_2 , Cl_2PtBr_2 and $[py_2N_2H_4]Cl_2PtCl_2$. Four groups of
 different substituents were investigated.

from the dichloride $[py_2N_2H_4]Cl_2PtCl_2$ by treating it with $NaNO_2$.
 J. Revlat Leach

Ph / na
 MT

Gel'man, A. D.

Preparation of potassium nitrochlorosulfonates.
A. D. Gel'man and L. M. Buzin. Proc. Acad. Sci. U.S.S.R.,
Ser. Chem. 107, 188-190 (1956) (Engl. translation).—See
C.A. 50, 15318a. B. M. R.

Chem 2

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GEL'MAN, A. D.

USSR/Inorganic Chemistry - Complex Compounds

C.

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4099

Author : Gel'man, A. D., Essen, D.N.

Inst : Academy of Sciences USSR

Title : Preparation of Nitrodichloro-Monoamino Platoate of Potassium

Orig Pub : Dokl. AN SSSR, 1956, 107, No 6, 835-836

Abstract : To prepare crystalline $K[PtNH_3ClNO_2Cl] \cdot H_2O$ (I) 1 mole of $NaNO_2$ was added to a warm aqueous solution of $K[PtNH_3Cl_3]$ (II). By addition of $[Pt(NH_3)_4]Cl_2$ to the reaction mixture a yellowish-orange precipitate of $[Pt(NH_3)_4][PtNH_3ClNO_2Cl]_2$ (III) was produced. Salt III was ground with water and there was added thereto a calculated amount of $K_2[PtCl_4]$. The Magnus salt that was formed was filtered off and the solution was evaporated at $50-60^\circ$ on a water bath. The residue was ground repeatedly with alcohol. Dried over $CaCl_2$ it

Card 1/2

- 15 -

GEL'MAN, A. D.

2/ The preparation of quadrivalent platinum complex compounds with two and six different substituents in the inner spheres of the trans and cis configurations. L. N. Essen and A. D. Gel'man. Doklady Akad. Nauk S.S.S.R. 163, 651-4, 1964, Acad. Sci. U.S.S.R. 108, Sect. Chem. Sci. (English translation) (1970) -- [PyNH₂CINO₂Pt] was obtained by the interaction of [PyNH₂Cl₂Pt] with the calc. amt. of NaNO₂. To a water suspension of the product, Br₂ was added dropwise, with a thorough agitation after each addn. The original mixt. changed through greenish-brown to brilliant yellow; the ppt. was filtered, analyzed, and its compn. was found to be [PyNH₂CINO₂Br₂Pt] (I). One Br was replaced with I by adding KI to a suspension of I in water, the mixt. heated for 20-25 min. on the water bath, the mixt. cooled, filtered, and the ppt. recrystd. from hot alc. Its compn. was found to be [PyNH₂CINO₂BrIPt] (II). Its structure was confirmed by its method of prepn. and by its re-^{action} to the bivalent Pt compd. [PyNO₂NH₂Cl₂Pt]. The cis compd. was obtained from the cis-[PyNO₂NH₂Cl₂Pt] by a similar oxidation with Br₂ and replacing one Br with I: [PyNO₂NH₂ClIPt] ^{Br₂} [PyNO₂NH₂ClBr₂Pt] ^{KI} [PyNO₂NH₂ClBrIPt]. The compd. obtained has the compn. of (II), but different phys. properties, therefore they are isomers. Structures are given for 3 stereoisomers of quadrivalent Pt complexes contg. six different ligands.

W. M. Sternberg

Inst-Phys-Chem, A.S. USSR

AUTHORS

Geiman A.D., Matorina N.N., Moskvina A.I.

89-10-4/36

TITLE

Determination of the Composition and Instability Constants of Pu³⁺ Oxalate Complexes.

(Opredeleniye sostava i konstant nestoykost'i oksalatnykh kompleksnykh ionov Pu³⁺) - Russian).

PERIODICAL

Atomnaya Energiya, 1957, Vol 3, Nr 10, pp 308 - 313 (U.S.S.R.)

ABSTRACT

The solubility of Pu₂(C₂O₄)₃·9H₂O in aqueous K₂C₂O₄-solution of the most various concentrations 0,01 - 2,4 Mol/l was measured at constant ionization of the solution and at a temperature of 20°C. Forming of Pu³⁺ complexes was proved and the following ion complexes were formed: [Pu(C₂O₄)₂]⁻, [Pu(C₂O₄)₃]⁻³ and [Pu(C₂O₄)₄]⁻⁵ with the instability constants:

4,9·10⁻¹⁰; 4,10 · 10⁻¹⁰ and 11,9·10⁻¹¹ respectively.

The solubility of Pu₂(C₂O₄)₃·9H₂O in an aqueous (NH₄)₂C₂O₄-solution at an ammonium concentration of 0,07 - 0,7 mol/l at a temperature of 70° C was also measured. The following ion complexes with the instability constants were found:

[Pu(C ₂ O ₄) ₂] ⁻	11,6·10 ⁻⁹
[Pu(C ₂ O ₄) ₃] ⁻³	5,6·10 ⁻⁹
[Pu(C ₂ O ₄) ₄] ⁻⁵	2,5·10 ⁻⁹

There are 4 figures, 3 tables and 7 Slavic references.

January, 1957
Library of Congress.

SUBMITTED
AVAILABLE

Card 1/1

Gel'man, A. D.
AUTHORS: Gel'man, A. D., Matorina, N. N. and
Moskvin, A. I.

20-1-23/42

TITLE: An Investigation of the Formation Conditions and of the Stability of Complex Oxalate Compounds of Pu (III) in Aqueous Solutions (Issledovaniye usloviy obrazovaniya i prochnosti oksalatnykh kompleksnykh soyedineniy Pu (III) v vodnykh rastvorakh).

PERIODICAL: Doklady AN SSSR, 1957, Vol. 117, Nr 1, pp. 88-91 (USER)

ABSTRACT: From other publications it is well known, that Pu (III) shows much less preference for the formation of complexes. The authors studied the stability of solutions of oxalate, carbonate, citrate and ethylene-diamine-tetra-acetate complex compounds of Pu (III) against oxydation by the oxygen of the air by spectral photometric methods. It appears, that Khindmen was correct with his assumption, that complex formation cannot cause a noticeable modification of the absorption spectrum of Pu (III). After the authors having established the conditions of the above-mentioned stability, they approached the problem of the determination of the composition and of the instability

Card 1/4

An Investigation of the Formation Conditions and of the
Stability of Complex Oxalate Compounds of Pu (III) in
Aqueous Solutions

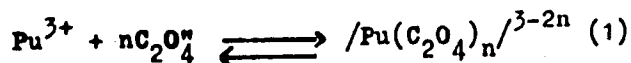
20-1-23/42

constant of the complex ions of PU (III) with various
complex constituents. Two methods were employed: a) the
method of solubility (at $\text{pH} \sim 8$) and b) the method of ion-
exchange (at $\text{pH} \sim 1.4 - 3.0$). a) At first the solubility of
 $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ in aqueous solutions of $\text{K}_2\text{C}_2\text{O}_4$ at 20°C
and at a constant ion density of the solution was
determined. Pu (III) was protected against oxydation by a
nitrogen jet. The plutonium contents of the solution were
determined by radiometric measurements. The results are
given in table 1, from which the composition and the general
instability constants (reference 6) of the oxalate complex
ions of Pu (III) were determined or computed, respectively.
In the range of concentration of $\text{K}_2\text{C}_2\text{O}_4$ under investigation
complex ions are formed (more exactly a relation between
Pu (III) and the $\text{C}_2\text{O}_4^{2-}$ -ion): $[\text{Pu}(\text{C}_2\text{O}_4)_2]^-$, $[\text{Pu}(\text{C}_2\text{O}_4)_3]^{3-}$ and
 $[\text{Pu}(\text{C}_2\text{O}_4)_4]^{5-}$, the total concentration instability constants

Card 2/4

An Investigation of the Formation Conditions and of the Stability of Complex Oxalate Compounds of Pu (III) in Aqueous Solutions 20-1-23/42

of which ("obshchiye kontsentratsionnyye konstanty nestoykosti"), corresponding to $4,9 \cdot 10^{-10}$; $4,1 \cdot 10^{-10}$ and $1,2 \cdot 10^{-10}$, are equal. The dependence of the concentration of the ions in question on the concentration of the complex constituent is illustrated in figure 1. In an analogous way the solubility of $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ in aqueous solutions of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in the range of concentration of the ammonium oxalate from 0.07 to 0.7 Mol/l at 70°C was determined (table 1). In this process complex ions of the same composition are formed, the total instability constants of which for $\text{Pu}_2(\text{C}_2\text{O}_4)_2^{4-}$ $11,6 \cdot 10^{-9}$, for $[\text{Pu}(\text{C}_2\text{O}_4)_3]^{3-}$ $5,6 \cdot 10^{-9}$, and for $[\text{Pu}(\text{C}_2\text{O}_4)_4]^{5-}$ $2,5 \cdot 10^{-9}$ are equal. The heat of formation of the complex ions in the case of the reaction



Card 3/4

was also computed. It was found, that ΔQ equals 1300 Kcal

Finally, the distribution of Pu (III) between the 1 molar solution of NH_4Cl and of "cationite" KU-2 (reference 15) was determined with respect to the pH-value of the solution (table 2). There are 2 figures, 2 tables and 1 figure.

APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R000514710001-2

ASSOCIATION: Institute for Physical Chemistry AN USSR (Institut fizicheskoy khimii Akademii nauk SSSR)

PRESENTED: June 24, 1957, by I. I. Chernyayev, Academician

SUBMITTED; June 13, 1957

AVAILABLE: Library of Congress

Card 4/4

Gelman, A.D.

7
 Coprecipitation of cerium by uranium(IV) oxalate. A. D. Gelman, *Zhur. Neorg. Khim.* 1, 1438-40 (1957). The copptn. of microquantities of radioactive Ce with the oxalate of U^{4+} was studied. Ce forms anomalous mixed crystals with the U oxalate. When the U compd. was pptd. without mixing, the Ce was carried down to a greater extent than that which corresponds to the equil. state and it does not obey the logarithmic law. In the system $U(C_2O_4)_2 \cdot Ce(C_2O_4)_2$ no lower limit was observed for the mixing, and the upper limit increases with an increase in the U concn.
 J. Rostar Leach

1-100
 1-100

1-100
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78-3-4-24/38

AUTHORS: Moskvina, A. I., Gel'man, A. D.

TITLE: Investigation of the Physico-Chemical Properties of Aqueous Solutions of Plutonium Oxalate (IV) and the Determination of Their Solubility Products (Issledovaniye fiziko-khimicheskikh svoystv vodnykh rastvorov oksalata plutoniya (IV) i opredeleniye yego proizvedeniya rastvorimosti)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 4, pp. 956-961 (USSR)

ABSTRACT: The solubility of plutonium-IV-oxalate in water and in the acids H_2SO_4 , HNO_3 and $HClO_4$ was determined. Based on the solubility of plutonium-IV-oxalate, the determination of the pH-value and the electric conductivity of the saturated aqueous solutions of $Pu(C_2O_4)_2 \cdot 6 H_2O$ it was found that the aqueous solutions of plutonium-IV-oxalate have acidic properties. In the saturated aqueous solution of $Pu(C_2O_4)_2 \cdot 6 H_2O$ the hydrogen-ion concentration $[H^+] = 3.98 \cdot 10^{-8}$. The dissociation constant of plutonium-IV-oxalate $= 2.7 \cdot 10^{-5}$. The solubility of $Pu(C_2O_4)_2 \cdot 6 H_2O$ decreases with the decrease of the pH-value of the solution. With an increase of the acid

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78-3-4-24/38

Investigation of the Physico-Chemical Properties of Aqueous Solutions of Plutonium Oxalate(IV) and the Determination of Their Solubility Products

concentration the solubility increases under the formation of complexes of Pu-IV with the anion of the corresponding acid. For the determination of the solubility product of $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{H}_2\text{O}$ a mixture of HNO_3 -(NH_4) $_2\text{C}_2\text{O}_4$ was used. The solubility product amounts to $4.10 \cdot 10^{-22}$.

This new method for the determination of the solubility products of difficultly soluble precipitates in acids is also used successfully in other systems, as for instance with $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{H}_2\text{O}$, $\text{UO}_2(\text{C}_2\text{O}_4) \cdot 3 \text{H}_2\text{O}$, and others. There are 2 figures, 5 tables, and 12 references, all of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR
(Institute for Physical Chemistry, AS USSR)

SUBMITTED: July 27, 1957

Card 2/2

OMEL'MAN, A.D.; MEYOD'YEVA, M.P.

Preparation of trivalent neptunium. Dokl. AN SSSR 117 no.2:225-226
N '57. (MIRA 11:3)

1. Institut fizicheskoy khimii Akademii nauk SSSR. Predstavleno
akademikom I.I. Chernyayevym.
(Neptunium)

AUTHORS: Ivanova, O. M., Gel'man, A. D. 78-3-6-9/30

TITLE: On the Amino Derivatives of Trimethyl Platinum
(Ob aminoproisvodnykh trimetilplatiny)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 6,
pp. 1334-1346 (USSR)

ABSTRACT: The properties of some organometallic compounds of platinum were investigated and the synthesis of the amino derivatives of trimethyl platinum was described. The following six mixed organometallic compounds of platinum were synthesized:
 $(\text{CH}_3)_3\text{PtOCH}_3$, $(\text{CH}_3)_3\text{PtBr}$, $[\text{Pt}(\text{CH}_3)_3(\text{NH}_3)_3]\text{Br}$,
 $[\text{Pt}(\text{CH}_3)_3(\text{NH}_3)_3]\text{Cl}$, $[\text{Pt}(\text{CH}_3)_3\text{Py}_2\text{Cl}]$, $[\text{Pt}(\text{CH}_3)_3\text{PyNH}_3\text{Z}]$.

A new synthesis of $(\text{CH}_3)_3\text{PtJ}$ was carried out by a reaction of $\text{CH}_3\cdot\text{MgJ}$ in benzene-ether solution with $\text{K}[\text{PtC}_3\text{H}_6\cdot\text{Cl}_3]$, $\text{K}_2[\text{PtCl}_6]$ and dehydrated Na_2PtCl_6 .

The best yield of $(\text{CH}_3)_3\text{PtJ}$ - approximately 55 %, was

Card 1/2

On the Amino Derivatives of Trimethyl Platinum

78-3-6-9/30

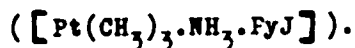
obtained with $(Na_2)_2 [PtCl_6]$. Due to the determination of the molecular weight of the compounds



it was found that these compounds are monomeric.

The reactions of trimethyl platinum compounds investigated show that the methyl group is immovable in these compounds. However, the amino group in the compounds of type $[Pt(CH_3)_3 \cdot (NH_3)_3] x$, on which occasion x represents J , Br or Cl , shows various mobility in dependence on the halide ion.

In the interaction of diamine- $[Pt(CH_3)_3 \cdot (NH_3)_2 \cdot J]$ with pyridine only one NH_3 group from the inner sphere of the complex can be exchanged by Py , namely under the formation of trimethyl amino pyridine iodine platinum



Card 2/3

There are 1 figure, 2 tables, and 14 references, 5 of which are Soviet.

On the Amino Derivatives of Trimethyl Platinum

ASSOCIATION: Institut khimicheskoy i neorganicheskoy fiziki im.
N. N. Kurnakova AN SSSR (Institute of General and Inorganic
Chemistry (Acad. N. N. Kurnakov, 125 080))

SUBMITTED: May 21, 1967

AVAILABLE: Library of Congress

1. Trimethyl platinum--Properties
2. Amino derivatives--Synthesis

Card 5/5

78-3-4-25/38

AUTHORS: Moskvin, A. I., Gel'man, A. D.

TITLE: Determination of the Composition and Instability Constants of Oxalate- and Carbonate Complexes of Plutonium-IV (Opredeleniye sostava i konstant nestoykosti oksalatnykh i karbonatnykh kompleksov plutoniya (IV))

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 4, pp. 962-974 (USSR)

ABSTRACT: The solubility of $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{H}_2\text{O}$ in solutions of ammonium oxalate of concentrations of from 0.001 - 0.35 mol/l in the presence of 1 mol HNO_3 were determined. Based on the achieved results the composition of the complexes as well as the stability of the oxalate complexes of Pu-IV were determined. For $[\text{Pu}(\text{C}_2\text{O}_4)]^{2+}$ $K_H = 1.8 \cdot 10^{-9}$, for $[\text{Pu}(\text{C}_2\text{O}_4)_2]^0 = 1.2 \cdot 10^{-17}$, for $[\text{Pu}(\text{C}_2\text{O}_4)_3]^{2-} = 4.0 \cdot 10^{-24}$, for $[\text{Pu}(\text{C}_2\text{O}_4)_4]^{4-} = 3.2 \cdot 10^{-28}$.

The solubility of plutonium-IV-hydroxide at constant ion-density in aqueous solutions of K_2CO_3 0.36-3.62 mol/l and at

Card 1/3

78-3-4-25/38

Determination of the Composition and Instability Constants of Oxalate- and Carbonate Complexes of Plutonium-IV

a temperature of 20°C was determined. Also the solubility of plutonium-IV-hydroxide in aqueous solutions of K_2CO_3 of various concentrations without constant ion-density³ was determined. It was found that with an increase of the concentration of K_2CO_3 the solubility of plutonium-IV-hydroxide increases under the formation of complexes of Pu-IV-carbonate. The carbonate complex of plutonium-IV has the following composition: $[Pu(CO_3)]^{2+}$ with an instability constant of $1,1 \cdot 10^{-47}$.

With carbonate complex solutions of plutonium-IV also the adsorption spectrum was determined and the existence of the carbonate complex was proved by that. The formation of plutonium-IV-carbonate complexes proceeds stepwise. In solutions there exist several plutonium-IV-carbonate solutions of various compositions. The tendency of plutonium of other valence to form complexes with oxalate was also investigated. The tendency to complex formation of plutonium has the following order: $Pu^{4+} > Pu^{3+} > Pu^{3+} > PuO_2^{2+} > PuO_2^+$.

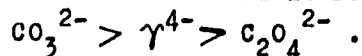
Card 2/3

78-3-4-25/38

Determination of the Composition and Instability Constants of Oxalate- and Carbonate Complexes of Plutonium-IV

The tendency of plutonium to form complexes with different anions CO_3^{2-} , $\text{C}_6\text{H}_5\text{O}_7^{3-}$, $\text{C}_4\text{H}_4\text{O}_6^{2-}$ has probably the same order as with oxalates.

Based on the instability constant of plutonium-IV with some complex partners the tendency to form complexes of Pu-IV-ions can be classified as follows:



γ^{4-} = anion of ethylene-diamine tetraacetic acid.

There are 5 figures, 7 tables, and 14 references, 11 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR
(Institute for Physical Chemistry, AS USSR)

SUBMITTED: July 27, 1957

Card 3 / 3

GELMAN, A. D.

AUTHORS: Gel'man, A. D., Sokhina, L. P.

78-3-5-2/32

TITLE: Oxalate Complexer of Plutonium-(IV) (Oksalatnyye kompleksnyye soyedineniya plutoniya(IV))

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol 3, Nr 5, pp 1100-1104 (USSR)

ABSTRACT: The oxalate complexes of plutonium-(IV) in solid phase have been isolated and their properties were examined in detail.
 $(\text{NH}_4)_6 [\text{Pu}(\text{C}_2\text{O}_4)_5]$, $\text{Na}_4 [\text{Pu}(\text{C}_2\text{O}_4)_4] \cdot 5\text{H}_2\text{O}$ were isolated as greenish yellow crystals. $\text{K}_4 [\text{Pu}(\text{C}_2\text{O}_4)_4] \cdot 4\text{H}_2\text{O}$ and $\text{K}_6 [\text{Pu}(\text{C}_2\text{O}_4)_5] \cdot 4\text{H}_2\text{O}$ were isolated and their existence proved by the determination of the electric conductivity. All plutonium compositions are soluble in water, and are stable in cold and in heat.
By the increase of the pH -value of the oxalate complex, solutions decomposition occurs and hydroxides precipitate as final products.

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The oxalate solutions of plutonium-(IV) are also

Oxalate Complexes of Plutonium-(IV)

78-3-5-8/39

decomposable by strong acidification.

The solid plutonium-(IV) oxalates modify if they are stored in air. This modification is connected with the destroying influence of α -rays upon the oxalate ion. By the influence of α -rays, the oxalate ion is decomposed into CO and CO₂.

There are 6 tables and 3 references, 2 of which are Soviet.

SUBMITTED: November 15, 1957

AVAILABLE: Library of Congress

1. Plutonium oxalate--Properties

Card 2/2

GELMAN, A. D.

AUTHORS: Gel'man, A. D., Drabkina, L. Ye. 78-3-5-9/39

TITLE: Production and Examination of the Properties of Some Oxalate Compounds of Hexavalent Plutonium (Polucheniye i issledovaniye svoystv nekotorykh oksalatnykh soyedineniy shestivalentnogo plutoniya)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol 3, Nr 5, pp 1105-1108 (USSR)

ABSTRACT: Plutonium oxalate was produced and the composition was found as $\text{PuO}_2(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$. The precipitated plutonium is at first light pink, and later changes into green. The solubility of plutonyl-oxalate in nitric acid was determined at different concentrations in the presence of oxalic acid and ammonium oxalate. The solubility of plutonyl oxalate in ammonium oxalate in presence of nitric acid favors the assumption that, thereby, soluble plutonium-(IV)-oxalate complexes are formed. The composition of the ammonium complex is represented by: $(\text{NH}_4)_2[\text{PuO}_2(\text{C}_2\text{O}_4)_2]$.

Card 1/2 In solutions of plutonyl oxalate in 1 n HNO_3 in presence

Production and Examination of the Properties of Some
Oxalate Compounds of Hexavalent Plutonium

78-3-5-9/39

of ammonium-oxalate, in addition, the following complexes
exist:

$[\text{PuO}_2\text{C}_2\text{O}_4]^0$ and $[\text{PuO}_2(\text{C}_2\text{O}_4)_2]^{2-}$ which have stability
constants of $2,2 \cdot 10^{-7}$ and $4,3 \cdot 10^{-12}$.

In aqueous solutions of ammonium- and potassium
oxalate, further complexes with a higher oxalate anion
content probably exist.

There are 2 figures, 4 tables, and 3 references, 2 of
which are Soviet.

SUBMITTED: November 15, 1957

AVAILABLE: Library of Congress

1. Plutonium oxalate--Properties
2. Complex compounds--Analysis
3. Ammonium oxalate--Chemical reactions

Card 2/2

78-3-6-5/30

AUTHORS: Gel'man, A. D., Zaytsev, L. M.

TITLE: Carbonate and Carbonate Oxalate Complexes of Plutonium-(IV)
I. Potassium Plutonium Carbonate (Karbonatnyye i karbonatno-
~~oksalatnyye kompleksy~~ soedineniya plutoniya (IV) I.
Plutoniyykarbonaty kaliya)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 6,
pp. 1304-1311 (USSR)

ABSTRACT: The synthesis for the production of solid carbonate complex compounds of plutonium-(IV) in greatest purity was elaborated. Solid plutonium-(IV)-oxalate was dissolved in potassium-, sodium-, and ammonia-carbonate as initial components. The solid complex compounds were isolated by ethyl alcohol. Also four carbonate complex compounds of plutonium-(IV) with potassium were investigated and the following formulae were determined for the compounds: $K_4[Pu(CO_3)_4] \cdot nH_2O$; $K_6[Pu(CO_3)_5] \cdot nH_2O$; $K_8[Pu(CO_3)_6] \cdot nH_2O$; $K_{12}[Pu(CO_3)_8] \cdot nH_2O$.
The microscopic investigations of the potassium carbonate complex compounds of plutonium confirm the crystalline structure of these compounds.

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Carbonate and Carbonate Oxalate Complexes of Plutonium-(IV) 78-3-6-5/30
I. Potassium Plutonium Carbonate

The investigations of the electric conductivity of the solutions show that the complex compound $K_{12}[Pu(CO_3)_8] \cdot nH_2O$ occurs in dissolved state.
It was found that the coordination number of the plutonium carbonate complex compounds is 8.
There are 8 tables and 15 references, 4 of which are Soviet.

SUBMITTED: November 15, 1957

AVAILABLE: Library of Congress

1. Plutonium compounds--Synthesis
2. Complex compounds--Production
3. Complex compounds--Synthesis

Card 2/2

SOV/78-3-7-15/44

AUTHORS:

Gel'man, A. D., Zaytsev, L. M.

TITLE:

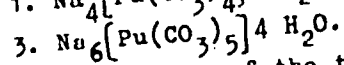
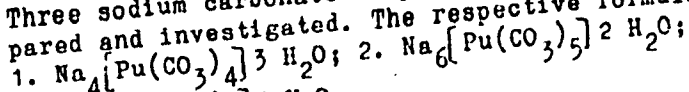
II. Sodium Plutonylcarbonates (II. Plutoniyykarbonaty natriya)

PERIODICAL:

Zhurnal neorganicheskoy khimii, 1958, Vol. 3, Nr 7, pp. 1551-1554 (USSR)

ABSTRACT:

The sodium plutonylcarbonate complex was produced and the dependence between the concentration of the solvents and the composition of the obtained complex compounds was determined. The optimum conditions for the production are an 18-20% soda solution and alcohol of 55-60%. In the alcoholic solution mentioned the sodium plutonylcarbonate complex compound has its lowest degree of solubility. By analysis of the solid phase it was found that the ratio Pu : CO₂ : Na is 1:4:4 and 1:5:6. Three sodium carbonate complex compounds of plutonium were prepared and investigated. The respective formulae are:



In the course of the thermal decomposition of $\text{Na}_4[\text{Pu}(\text{CO}_3)_4] \cdot 3 \text{H}_2\text{O}$

Card 1/2

II. Sodium.Plutonylcarbonates

SOV/78-3-7-15/44

It was found that at 300-400°C 3 mol H₂O and 2 mol CO₂ are separated. The crystals retain their shape. The second compound produces large green crystals which, when being dehydrated, go over into a fine greenish-yellow crystal powder. The third compound is more stable. There are 3 figures and 3 tables.

SUBMITTED: November 15, 1957

1. Complex compounds--Solubility 2. Complex compounds--Chemical analysis 3. Complex compounds--Properties 4. Plutonium--Properties Sodium--Properties

Card 2/2

AUTHORS: Gel'man, A.D., Zaytsev, L.M.

304/ 78-3-7-16/44

TITLE: III. Mixed Oxalate-Carbonate Compounds of Plutonium (IV)
(III. Smeshannyye oksalatno-karbonatnyye soyedineniya plutoniya (IV))

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 7, pp 1555-1564 (USSR)

ABSTRACT: Mixed oxalate-carbonate compounds of plutonium (IV) were synthesized and investigated. The following compounds were produced: $K_2[Pu(CO_3)_2C_2O_4] \cdot nH_2O$; $Na_4[Pu(CO_3)_2(C_2O_4)_2] \cdot 3H_2O$; $Na_4[Pu(CO_3)_3(C_2O_4)] \cdot nH_2O$; $K_4[Pu(CO_3)_3C_2O_4] \cdot nH_2O$; $K_6[Pu(C_2O_4)_3C_2O_4] \cdot nH_2O$; $K_{10}[Pu(C_2O_4)_4(C_2O_4)_3] \cdot nH_2O$; $K_{12}[Pu(CO_3)(C_2O_4)_7] \cdot nH_2O$.

By crystal optics and X-ray analysis it is shown that the production and composition of the aforementioned complex compounds depend on the concentration of the sodium carbonate. The complex compounds existing in the solution depend on the concentration of the oxalate- and carbonate ions. It is shown that in the

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III. Mixed Oxalate-Carbonate Compounds of
Plutonium (IV)

SOV/ 78-3-7-16/44

solution complicated complex compounds occur which decompose
with generation of the solid phase.

The aqueous solutions are unstable. As a result of the decomposition of the complexes plutonium-hydroxide is precipitated. Several problems connected with the structure of the products investigated are explained. There are 16 tables.

SUBMITTED: November 15, 1957

1. Complex compounds--Synthesis
2. Complex compounds--Chemical analysis
3. Complex compounds--Properties
4. Plutonium hydroxide--Precipitation

Card 2/2

SCY/78-3-8-34/48

AUTHORS: Drabkina, L. Ye., Moskvina, A. I., Gel'man, A. D.

TITLE: Determination of the Solubility Product of Plutonyl Oxalate
(Opredeleniye proizvedeniya rastvorimosti plutoniloksalata)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol. 3, Nr 8, pp. 1934-1936 (USSR)

ABSTRACT: The solubility product was determined of plutonyl oxalate in 1,1, 2,0, 3,08 mol. HNO_3 and in mixtures of HNO_3 - $\text{H}_2\text{C}_2\text{O}_4$. The solubility product of plutonyl oxalate has an average value of $6,0 \cdot 10^{-10}$. With an increase of the oxalic acid concentration the solubility of plutonyl oxalate decreases. Approximate values of the solubility product of plutonyl oxalate were also determined by means of the graphical method from data on the solubility of plutonyl oxalate in mixed solutions of HNO_3 -(NH_4) $_2\text{C}_2\text{O}_4$. The solubility product, determined by the graphical method, amounts to $1,4 \cdot 10^{-10}$. This value corresponds quite well to the value found in the experimental way. There are 1 figure, 2 tables, and 10 references, 9 of which are

Card 1/2

SOV/78-3-8-34/48

Determination of the Solubility Product of Plutonyl Oxalate

Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of
Physical Chemistry, AS USSR)

SUBMITTED: October 31, 1957

Card 2/2

GEL'MAN, A D

89-3-5/30

AUTHORS: Gel'man, A. D. , Mefod'yeva, M. P.

TITLE: The Reduction of Neptunium to the Trivalent State by a Chemical Method (O vosstanovlenii neptuniya do trekhvalentnogo sostoyaniya khimicheskim metodom)

PERIODICAL: Atomnaya Energiya, 1958, Vol. 4, Nr 3, pp. 271 - 274 (USSR)

ABSTRACT: By means of the spectrographic method it was found that in a 1 to 1,5 M nitric acid and hydrochloric acid solution of rongalite ($\text{NaHSO}_2 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$), neptunium (IV) is reduced to Np(III) . The reduction takes place in nitrogen atmosphere as well as in air. The degree of reduction as well as the stability of Np(III) are, however, remarkably increased in a nitrogen atmosphere. It was found that by an increase of the general content of the reducing agent in the solution (hydrasin + rongalite) the reduction to Np(III) is favored. The reduction of neptunium is on the average accomplished to 70 % in nitric acid solution but to 95 % in hydrochloric acid solution.

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It was further found that in the reduction of Np(V) in ron-

89-3-5/30

The Reduction of Neptunium to the Trivalent State by a Chemical Method

galite a mixture of Np(III) + Np(IV) is formed. Np(III) shows a considerable stability against oxidation by atmospheric oxygen in the mixture of Np(IV) with Np(III) . There are 4 figures, and 4 references, 1 of which is Slavic.

SUBMITTED: January 19, 1957

AVAILABLE: Library of Congress

1. Neptunium-Reduction 2. Spectographic method-Application

Card 2/2

AUTHORS: Gel'man, A. D., Moskvina, A. I.

20-3-21/59

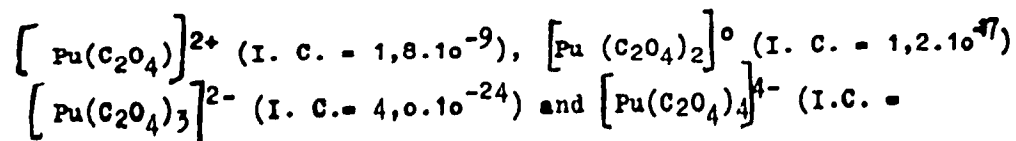
TITLE: An Investigation of the Complex Oxalates and Carbonates of Plutonium /IV/ in Water Solutions by Means of the Solubility Method (Issledovaniye oksalatnykh i karbozatnykh kompleksov plutoniya (IV) v vodnykh rastvorakh metodom rastvorimosti).

PERIODICAL: Doklady AN SSSR, 1958, Vol. 118, Nr 3, pp. 493-496 (USSR)

ABSTRACT: No data can be found in publications concerning the composition and stability of the carbonates complex of plutonium (IV). In this work the authors give the determination of the composition as well as of the instability constants of Pu (IV) as mentioned in the title. 4-6 hours are sufficient to reach the equilibrium between the ammonium-oxalate solution and the solid phase of Pu (IV) oxalate at $20 \pm 0,02^\circ$. The experimental results are mentioned in table 1. The solubility of Pu (IV) oxalate decreases with the increase of the concentration of ammonium-oxalate from 0,001 to 0,005 Mol/liter, it reaches a minimum of $3,55 \cdot 10^{-5}$ mol. Pu(IV) per liter and then increases because of the complex formation of Pu(IV) with oxalations. The solubility is expressed by means of an equation (1). Complex ions with general instability constants (β I. C. in brackets) are formed:

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An Investigation of the Complex Oxalates and Carbonates of Plutonium /IV/ in Water Solutions by Means of the Solubility Method. 20-3-21/59



$= 3,3 \cdot 10^{-28}$). These constants correspond to a complete decomposition of the ions of Pu(IV). From these general instability constants the stepwise constants were determined. Both kinds of constants correspond to different decomposition schemes (2) and (3). Table 2 gives the solubility of Pu(IV)-oxalate in water and in H_2SO_4 , HNO_3 and HClO_4 . From this follows that the solubility, but that then, starting from 0,1 N, it increases again. Because of their interaction with the oxalate in aqueous solutions the acids form a series: $\text{H}_2\text{SO}_4 \gg \text{HNO}_3 \gg \text{HClO}_4$. The pH of a saturated Pu(IV) oxalate solution was equal to 4,4, the molecular electric conductivity $470 \Omega^{-1}$. The dissociation process of Pu(IV) oxalate is explained by means of a scheme for its analogy with U^{4+} . The estimated constant of the acid dissoziation of Pu(IV) gave $\sim 3 \cdot 10^{-5}$. Furtheron the solubility of Pu(IV) oxalate in a mixed solution HNO_3 - $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (table 1), as well as of Pu(IV) hydroxide in K_2CO_3 with a constant ionic density with an addition of NaCl and KClO_4 (table 3) are measured. From tabl. 3 it

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An Investigation of the Complex Oxalates and Carbonates of Plutonium /IV/ in Water Solutions by Means of the Solubility Method. 20-5-21/59

can be seen that the solubility of the hydroxide increases with the increasing K_2CO_3 concentration because of the complex formation of Pu(IV) with Carbonate ions. The complex ion $[Pu(CO_3)_2]^{2+}$ has an instability coefficient of the concentration $1,1 \cdot 10^{-47}$. Absorption spectra of the solutions of the latter complex were investigated. Table 4 gives the calculated values of the ion potential. From this is seen the tendency for complex formation of single plutonium ions: $Pu^{4+} < Pu^{3+} \approx PuO_2^{2+} < PuO_2^+$, which decreases with the decreases of the ion potential. By means of the data in table 5 the anions can be arranged in a series according to their tendency for complex formation with Pu(IV): $CO_3^{2-} > C_4H_4O_6^{2-} > C_6H_5O_7^{3-} \approx C_2O_4^{2-}$. There are 5 tables, 5 references, 4 of which are Slavic.

ASSOCIATION: Institute for Physical Chemistry AN USSR (Institut fizicheskoy khimii Akademii nauk SSSR).
PRESENTED: August 15, 1957, by I. I. Chernyayev, Academician
SUBMITTED: August 1, 1957
AVAILABLE: Library of Congress
Card 3/3

SOV/20-120-1-25/63

AUTHORS: Artyukhin, P. I., Gel'man, A. D., Medvedovskiy, V. I.

TITLE: Investigation of the Redox Potentials of Plutonium in Nitric Acid (Issledovaniye okislitel'no-vosstanovitel'nykh potentsialov plutoniya v azotnoy kislote)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 1, pp. 98-100 (USSR)

ABSTRACT: The authors determined the formal redox potentials of various plutonium pairs in nitric acid solutions of different concentrations, as well as the disproportionating of Pu (IV) in nitric acid solutions. The potentials of the pair Pu(IV) - Pu(III) were measured at 25° in a carefully purified nitrogen atmosphere by means of an apparatus already described earlier (Ref 10). These measurements were carried out within the whole range of the ratios of the concentrations of Pu(IV) and Pu(III). The experiments of the direct determination of the potentials of the pairs Pu(VI) - Pu(IV) did not turn out to be successful. The measurement of the formal potentials of the pair Pu(VI) - Pu (IV) was carried out by

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Investigation of the Redox Potentials of Plutonium in Nitric Acid

SOV 20-120-1-25/63

disproportionating of Pu(IV) at low concentrations of nitric acid. This disproportionating of Pu(IV) was carried out at 25°. From the redox potentials measured on conditions of equilibrium and from the values of equilibrium concentrations the formal potentials for the pairs Pu(IV) - Pu(III), Pu(VI) - Pu(IV) and Pu(VI) - Pu(III) are calculated and given in a table. The formal potentials of the pairs Pu(VI) - Pu(IV), Pu(VI) - Pu(III) highly increase with increasing concentration of the hydrogen ions. The potentials of these pairs depend as the fourth power on the concentrations of the ions H^+ . The reactions taking place at the electrode are written down. Using these equations the formal potentials of the pairs Pu(VI) - Pu(IV) and Pu(VI) - Pu(III) in 1 N HNO_3 are calculated. The results obtained agree well with those of other authors. Proceeding from the discussed considerations schemes for the formal potentials of plutonium in nitric acid solutions are proposed and given. A diagram shows the changes of the concentrations of Pu(III), Pu(IV) and Pu(VI) with progressing time in 0,40 N HNO_3 . In spite of the existing complex formation of Pu(IV) the constants of the velocity of the disproportionating of Pu(IV) in nitric acid

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SOV/20-120-1-25/63

Investigation of the Redox Potentials of Plutonium in Nitric Acid

obtained are the same as in hydrochloric acid. There are 1 figure, 3 tables, and 15 references, 3 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR
(Institute of Physical Chemistry AS USSR)

PRESENTED: December 24, 1957, by I. I. Chernyayev, Member, Academy of Sciences, USSR

SUBMITTED: December 24, 1957

1. Plutonium--Analysis
2. Oxidation-reduction reactions
3. Nitric acid--Applications

Card 3/3

AUTHORS: Gel'man, A.D., Drabkina, L.Ye., Moskvina, A.I. SOV 78-3-7-14/44

TITLE: The Determination of the Composition and of the Instability Constants of the Oxalate Complex Ions of Plutonium (VI)
(Opredeleeniye sostava i konstant nestoykosti oksalatnykh komplekanykh ionov plutoniya (VI))

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 7, pp 1546-1550 (USSR)

ABSTRACT: In the present paper the results obtained in connection with the determination of the composition and the instability constants of oxalate complexes of PuO_2^{2+} by the solubility of plutonium (VI) oxalate in HNO_3 in the presence of ammonium oxalate are given. The determination of the solubility of plutonyl oxalate in nitric acid in the presence of ammonium oxalate was carried out at 20°C , and a value of $(3.5 \pm 0.3) \cdot 10^{-3}$ mol/l plutonyl oxalate was obtained. Solubility increases with an increase of the ammonium oxalate concentration because complexes are formed. The solubility product of $\text{PuO}_2 \cdot \text{C}_2\text{O}_4 \cdot 3 \text{H}_2\text{O} \approx (5.5) \cdot 10^{-10}$.

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The Determination of the Composition and of the Instability Constants of the Oxalate Complex Ions of Plutonium (VI)

In oxalate solutions of plutonium (VI) the following complexes exist: $[\text{PuO}_2(\text{C}_2\text{O}_4)]^0$ and $[\text{PuO}_2(\text{C}_2\text{O}_4)_2]^{2-}$. Their instability constants are: $(2.3) \cdot 10^{-7}$ and $(3.4 \dots 4.3) \cdot 10^{-12}$ respectively. There are 1 figures, 1 table, and 5 references, 4 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii, Akademii nauk SSSR (Institute of Physical Chemistry, AS USSR)

SUBMITTED: October 31, 1957

1. Complex ions--Stability
2. Complex ions--Solubility
3. Ammonium oxalate--Applications

Card 2/2

SOV/78-3-12-11/36

AUTHORS: Essen, L. N., Zakharova, F. A., Gel'man, A. D.

TITLE: Concerning the Synthesis of Isomers With Six Different Addenda
(K sintezu isomero v shest'yu razlichnymi zamestitelyami)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 12,
pp 2654-2661 (USSR)

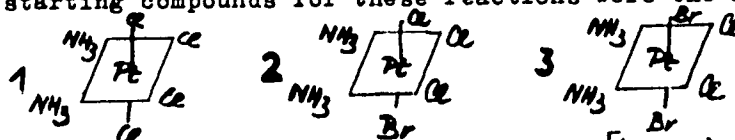
ABSTRACT: $[PyNH_3BrNO_2ClPt]$ and $[PyClNH_3NO_2BrPt]$, two geometric isomers with six different addenda, were synthesized. The starting material for the synthesis of the trans isomers was $[PyNH_3BrNO_2Pt]$, containing divalent platinum. The compound was first treated with $NaNO_2$, then with chlorine, and finally converted to the trans form $[PyNH_3BrNO_2ClPt]$ by treating with potassium iodide. This product has a dark green color, and has a solubility in water of 0.05 grams per 100 grams solution. A decomposition with the generation of iodine takes place at 200° when it is heated in open capillary tubes. The synthesis of the cis isomer $[PyClNH_3NO_2BrPt]$ was carried out using the salt

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SOV/78-3-12-11/36

Concerning the Synthesis of Isomers With Six Different Addenda

$K[PtPyCl_3]$. At 40-60°C in aqueous solution the NO_2 group containing an equivalent amount of sodium nitrite was added to the salt. The compound was then oxidized with bromine and the produced salt converted to the cis isomer with six addenda by reaction with potassium iodide. The cis isomer is a fine crystalline powder with a dark brown color, and melts without decomposition at 200°C. It has a solubility in water at 25° of 0.095 grams per 100 grams solution. The syntheses of isomers with two, three, and eight addenda were not successful, because the addition of the NO_2 group to the tetravalent platinum compound is extremely complicated. A few exchange reactions involving simple platinum (IV) compounds were carried out. The starting compounds for these reactions were the following:



By reacting potassium bromide with the $[(NH_3Cl)_2Cl_2Pt]$ salt in the ratio 1:1 the displacement of one chlorine in the co-

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SOV/78-3-12-11/36

Concerning the Synthesis of Isomers With Six Different Addenda

ordinates Cl-Pt-Cl takes place. By reacting 2 moles of KBr with one mole of $[(\text{NH}_3\text{Cl})_2\text{Cl}_2\text{Pt}]$ an exchange of the two chlorine atoms with bromine takes place under development of $[(\text{NH}_3\text{Cl})_2\text{Br}_2\text{Pt}]$. The bromine ion in the coordinates Br-Pt-Br could not be displaced by reaction with KCl. The experimental results show that chlorine and bromine have different coordination affinities in the inner spheres of tetravalent platinum compounds. An exchange of chlorine and bromine with the NO_2 group in the coordinates Br-Pt-Br, Br-Pt-Cl, and Cl-Pt-Cl did not occur. The course of the exchange reactions in the inner spheres of tetravalent platinum compounds is dependent upon the various coordination mobilities of the addenda. There are 11 Soviet references.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences, USSR)

Card 3/4 :

SOV/78-3-12-11/36

Concerning the Synthesis of Isomers With Six Different Addenda

SUBMITTED: August 5, 1957

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GEL'man, A. D.

AUTHORS: Gel'man, A. D., Matorina, N. N., Moskvina, A. I. 89-16/29
 TITLE: The Determination of the Composition and the Instability Constant of Oxalate Complexes of Pu^{+3} Compounds by the Method of Ion Exchange (Opredeleniye sostava i konstant nestoykosti oksalatnykh kompleksov Pu^{+3} metodom ionnogo obmena).

PERIODICAL: Atomnaya Energiya, 1958, Vol. 4, Nr 1, pp. 52 - 56 (USSR).

ABSTRACT: By the method of ion exchange the formation of ion complexes of Pu^{+3} in oxalate solutions was determined, and the pH value of the solutions was found to fluctuate between 1.4 and 2.8. Measuring results:
 1.) The instability constant of the complex ion $[Pu(C_2O_4)_2]^-$ is practically constant with in the range of the pH values from 1.47 to 2.65 (all values).
 2.) In a solution with $pH > 1.7$ a mixture of complex ions $[Pu(C_4O_7)_2]^-$ and $[Pu(HC_2O_4)_4]^-$ is developed, and the average instability constants for these two types of ions were measured to be $K'_H = 7.1 \cdot 10^{-10}$ and $K'' = 1.1 \cdot 10^{-11}$.

Card 1/2 3.) The constants K'_H and K''_H correspond to a total decay of the

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GEL'MAN A. D.

5(4)

AUTHORS:

Babushkin, A. A., Gribov, L. A.,
Gel'man, A. D.

SOV/20-123-3-22/54

TITLE:

The Nature of the Bond Between the Central Atom and Some Unsaturated Molecules in Complex Platinum Compounds (O kharaktere svyazi mezhdru tsentral'nyu atomom i nekotorymi nenasyshchennymi molekulami v kompleksnykh soyedineniyakh platiny)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 3, pp 461-463 (USSR)

ABSTRACT:

The problem of the bond between metals and the molecule mentioned in the title was investigated in numerous papers. A respective survey is given in reference 1. According to A. D. Gel'man (Ref 2) the platinum atom represents at the same time an electron donor and acceptor. In consequence of this a covalent double bond results between the central atom and the olefin. Chatt and Duncanson (Ref 4) suggest a scheme for this bond which can be regarded as π -electron interaction. The authors do not agree to the interpretation of the spectra observed. Chatt and Duncanson (and Ref 5, according to them) conclude from their interpretation that the double bond of the

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The Nature of the Bond Between the Central Atom
and Some Unsaturated Molecules in Complex Platinum Compounds

SOV/20-123-3-22/54

olefin is maintained also in the complex formation. The authors state, however, that the reasons for this fact are not sufficient. The purpose of their paper was therefore to perform a critical analysis of the infrared spectra of complex platinum compounds with ethylene, propylene and carbon monoxide: 1) contrary to reference 4, the frequencies in the range above 3000 cm^{-1} are a necessary but by no means sufficient proof of the maintenance of the double bond $\text{C}=\text{C}$ in the olefin part of the complex. Due to the similarity of the electron configuration in the CH_2 -group of the ethylene, ethylene oxide and cyclopropane molecules the authors suppose that the olefin is forming with platinum a compound according to the type of a triangular cyclic structure. 2) According to the above-mentioned statements it is more correct to attribute the frequencies of the ethylene and propylene complexes with platinum in the range $1490\text{--}1510\text{ cm}^{-1}$ to the deformation oscillation CH_2 (Ref 7a), but not to the frequency of valence oscillations of the double bond $\text{C}=\text{C}$. 3) The frequency of the non-plane

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The Nature of the Bond Between the Central Atom and Some Unsaturated Molecules in Complex Platinum Compounds

SOV/20-123-3-22/54

deformation oscillations of the CH-group is a typical feature of olefins (Ref 8). The absence of this frequency in the complex compound under consideration and the presence of 4 additional intense frequencies between 1300 and 700 cm^{-1} (as compared with the spectra of the initial addenda) proves a considerable transformation of the ethylene molecule that must be related with the transformation of the double bond $\text{C}=\text{C}$ into a single one. 4) The above-mentioned considerations are in accordance with the data on the structure of the complex compound mentioned (Ref 9). According to these data, the ethylene molecule is vertical to the PtCl_3 -plane and, shows with respect to the latter, nearly a symmetric position. The distance between the carbon atoms $d = 1.50 \text{ \AA}$ is a value characteristic of a single bond between these atoms. 5) The analysis of the infrared spectrum of the complex compound proves that the double bond $\text{C}=\text{C}$ in ethylene is transformed into a single one on the entrance of the platinum atom into the inner sphere. Therein the strength of the bond between

Card 3/4

The Nature of the Bond Between the Central Atom and Some Unsaturated Molecules in Complex Platinum Compounds SOV/20-123-3-22/54

platinum and the carbon atoms is according to the order of magnitude of the strength identical with an ordinary covalent bond. 6) The statements made in points 1-3 are valid both for $K[PtC_2H_4Cl_3] \cdot H_2O$ and $K[PtC_3H_6Cl_3] \cdot H_2O$. For this reason the authors claim that the structure and nature of the formation of the propylene bond with the central atom are similar to those of ethylene with platinum. There are 10 references, 5 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences USSR)

PRESENTED: July 7, 1958, by V. I. Spitsyn, Academician

SUBMITTED: June 26, 1958

Card 4/4

5(4), 21(1)
AUTHORS:

SOV/78-4-6-19/44
Gel'man, A. D., Artyukhin, P. I., Moskvina, A. I.

TITLE:

Investigation of the Complex Formation of Pentavalent Plutonium in Ethylene-diamine-tetraacetic Acid by the Ion Exchange Method (Issledovaniye kompleksobrazovaniya pyativalentnogo plutoniya v etilondiamintetraatsetatnykh rastvorakh metodom ionnogo obmena)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 6, pp 1332-1335 (USSR)

ABSTRACT:

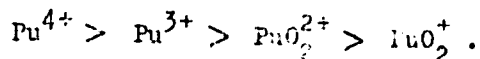
The complex formation process of Pu(V) in ethylene-diamine-tetraacetic acid was investigated by the ion exchange method. The results of the distribution of the pentavalent plutonium between 0.05 mol-solution NH_4Cl and the cation exchanger with different pH-value are given in table 1. They show that the complex ion $\text{PuO}_2\text{Y}^{3-}$ is produced in the pH-range 4 - 5 with the instability constant $6.3 \cdot 10^{-11}$. The influence of the pH-value on the distribution of Pu(V) between 0.05 mol solution NH_4Cl and the ion exchanger in the case of presence and absence of Komplexon is given in figure 1. The instability

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SOV/78-4-6-19/44

Investigation of the Complex Formation of Pentavalent Plutonium in Ethylene-diamine-tetraacetic Acid by the Ion Exchange Method

constants of the ADTA-complex ions of Pu(III), Pu(VI) and Pu(V) were compared and given in table 3. The inclination of different plutonium ions to complex formation has the following series:



The Pu(IV)-ion and the smaller Pu(V)-ion are most inclined to complex formation with the anion Y^{4-} . There are 2 figures, 3 tables, and 7 references, 4 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR
(Institute of Physical Chemistry of the Academy of Sciences, USSR)

SUBMITTED: April 16, 1958

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SOV/78-4-12-6/35

5(2) 5.2200(4)

AUTHORS: Gel'man, A. D., Zaytsev, L. M.

TITLE: Simple and Complex Carbonate Compounds of Plutonium (IV)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 12, pp 2688-2696 (USSR)

ABSTRACT: In an earlier paper (Ref 3) the authors reported on potassium- and sodium-plutonium carbonates. The present article treats of the corresponding complex ammonia compounds of tetravalent Pu. The soluble carbonate complexes of Pu(IV) were obtained by reducing the Pu(VI) tricarbonate with H_2O_2 in 10% ammonium carbonate solution. When pouring the solution into 75-80% methyl- or ethyl alcohol the green complex was precipitated in the form of sirup and could be dried by decantation and washing with absolute alcohol. Complete dehydration failed as decomposition occurred. The analysis had therefore to be made by means of an aqueous substance. It showed the composition $(NH_4)_6[Pu(CO_3)_5]nH_2O$. Storing in alcohol for some time or drying in air effected decomposition with brown coloring. Thermal analysis of the decomposed product indicated the absence of hydroxyl groups so that the composition of $PuO_2 \cdot PuOCO_3 \cdot 3H_2O$ was

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Simple and Complex Carbonate Compounds of Plutonium (IV)

ascribed to it. To prevent rapid decomposition of the green complex salt, it was stored in the exsiccator in the presence of ammonium carbonate and thus only partially decomposed to form the compound $(\text{NH}_4)_4[\text{Pu}(\text{CO}_3)_4] \cdot n\text{H}_2\text{O}$. When the hexavalent Pu compound is reduced in ammonium carbonate solution of high concentration (30% at 35°), the compound $(\text{NH}_4)_8[\text{Pu}(\text{CO}_3)_6] \cdot n\text{H}_2\text{O}$ is formed, which is also green. All of the three resulting complex compounds form green solutions in water, which decompose after a few minutes to separate green amorphous plutonium hydroxide. When studying the compound $(\text{NH}_4)_4[\text{Pu}(\text{CO}_3)_4] \cdot 4\text{H}_2\text{O}$ it was found that the change in the pH of its aqueous solution sets in only after 5-8 min. Meanwhile it was possible to measure the apparent molecular weight and electrical conductivity. The complex dissociated to form 5 ions, the apparent molecular weight being 113.0. Since the calculated molecular weight is 623, this dissociation was confirmed. The deviation ($623 : 113 \approx 5.5$) is caused by the beginning decomposition. The complex compounds can be longer stored in ammonium carbonate solutions than in pure water. Thermal analysis was carried out at low temperature

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Simple and Complex Carbonate Compounds of Plutonium (IV)

according to G. G. Tsurinov's method (Ref 4). The compound $(\text{NH}_4)_6[\text{Pu}(\text{CO}_3)_5] \cdot n\text{H}_2\text{O}$ splits off one ammonium carbonate molecule at 58° . Partial dehydration occurs at 70° . At 80° the compound $(\text{NH}_4)_4[\text{Pu}(\text{CO}_3)_4] \cdot 4\text{H}_2\text{O}$ decomposes to form $\text{PuO}_2 \cdot \text{PuOCO}_3$, and at 110° the basic oxycarbonate decomposes to yield PuO_2 . The slow decomposition of plutonium tetracarbonate in the air, however, leads to the compound $\text{PuOCO}_3 \cdot 2\text{H}_2\text{O}$. When heating the solutions of the Pu complex compounds, the compound $2.5\text{PuO}_2 \cdot \text{PuOCO}_3 \cdot 5.5\text{H}_2\text{O}$ is precipitated. The normal plutonium carbonate $\text{Pu}(\text{CO}_3)_2 \cdot n\text{H}_2\text{O}$ could not be obtained. There are 4 figures, 10 tables, and 4 references, 3 of which are Soviet.

SUBMITTED: September 9, 1958

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5(2) 21(1)

SOV/89-7-2-11/24

AUTHORS:

Gel'man, A. D., Moskvina, A. I., Artyukhin, P. I.

TITLE:

The Compositions and Dissociation Constants of Pu(V) and Pu(III) Complexes with Ethylenediaminetetraacetic Acid (Sostav i konstanty dissotsiatsii kompleksov Pu(V) i Pu(III) s etilendiamintetrauksusnoy kislotoy)

PERIODICAL: Atomnaya energiya, 1959, Vol 7, Nr 2, pp 162 - 163 (USSR)

ABSTRACT:

The complex formation of Pu(V) with and without complex-forming ethylene diamine tetra acetic acid (EDTA) was measured with the ion exchange method under the following conditions: KU-2; pH range 3.3 to 5.1; ionic force $\mu = 0.05$ (0.05 M NH_4Cl solution); temperature $20 \pm 1^\circ\text{C}$. In the examined pH range a complex ion of the type $\text{PuO}_2\text{Y}^{3-}$ (Y^{4-} - anion of the EDTA) is formed with a dissociation constant $K 6.8 \cdot 10^{-11}$. Similarly the complex formation was determined for Pu(III) in the pH range 1.2 to 3.4, in a nitrogen atmosphere $\mu = 1$ (1 M NH_4Cl). The following complex ions are formed: PuY^- and PuHY ; their dissociation constants are $4.4 \cdot 10^{-18}$ and $6.2 \cdot 10^{-10}$. By this and earlier data the dissociation constants of the EDTA complexes of the

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The Compositions and Dissociation Constants of Pu(V) and Pu(III) Complexes with Ethylenediaminetetraacetic Acid SOV/89-7-2-11/24

trivalent transuranic elements (Pu-Cf) can be compared and one may see that with increase of the Z the strength of the complexes of the type MY⁻ increases, which is easy to understand because of the increase of the ion potential. When the dissociation constants of the complex plutonium ions are being compared it can be established that the tendency of complex formation decreases in the following sequence:

$$\text{Pu}^{4+} > \text{Pu}^{3+} > \text{PuO}_2^{2+} > \text{PuO}_2^+$$
 i. e. with decrease of the ion potential.
 There are 1 table and 6 references, 4 of which are Soviet.

SUBMITTED: January 6, 1959

Card 2/2

5(2, 3)
AUTHORS:

Gel'man, A. D., Mefod'yeva, M. P.

SOV/20-124-4-24/67

TITLE:

On the Complex Formation of Np^{4+} and NpO_2^+ With Trilon B
in Aqueous Solutions (O kompleksoobrazovanii Np^{4+} i NpO_2^+ s
trilonom B v vodnykh rastvorakh)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124. Nr 4,
pp 815-818 (USSR)

ABSTRACT:

In spite of several investigations of the interaction of actinides with Trilon B (disodium salt of ethylene diamine tetraacetic acid) there are no data in publications available on the subject under review. The authors tried to fill the gap. A. Complex formation of Np^{4+} with trilon Z.

Addition of excess trilon Z to the Np(IV) -solution at pH 5.5 shifts the absorption intensity toward the long-wave range; instead of a maximum 722 $\text{m}\mu$, 740 $\text{m}\mu$ appears and a second one at 780 $\text{m}\mu$. The maximum 960 $\text{m}\mu$ is shifted up to 983 $\text{m}\mu$. pH increase up to 6.8 leads to a reduction of the maxima 740 and 780 $\text{m}\mu$ with time, while instead of 983 a maximum

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SOV/20-124-4-24/57

On the Complex Formation of Np^{4+} and NpO_2^+ With
Trilon B in Aqueous Solutions

appears at 988 $\text{m}\mu$. A decrease of the pH values down to 5.2 and below led to a reverse process (Fig 1). On the curves of figure 2 2 horizontal sections (plateaus) can be read: 1) between 0.5 n HCl and pH 2; 2) from pH 3.5 to 6.5 of the solution in which the complex formation was investigated. Apparently: only one single complex compound predominates in each of both ranges. The composition, i. e. the ratio

$[\text{Np}^{4+}]$ in the complex was determined by spectrophotometric titration of Np^{4+} solution with Trilon (at constant acidity and $\mu = 1$). The authors calculated the stability constants for all complexes which could be produced within the system (provided one of them is present at the respective moment). As follows from table 1, a stationary stability constant within the whole range of acidity is attained most favorably for $[\text{NpH}_3\text{Y}]^{3+}$ and $[\text{NpH}_2\text{Y}]^{2+}$. It is not possible to determine the presence of 2 different complexes according to experimental data.

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